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AND

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## ERRATA.

| Page. | Lines. | Corrections. |
|---|---|---|
| 73 | 11 from bottom .. | *for* $NH_3$, *read* $NH_2$. |
| 110 | 26 and 31, from top .. | „ manganic, *read* margaric. |
| 544 | 1 and 5, „ .. | „ nitric, *read* nitrous. |

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## ERRATUM.

Page 110, lines 26 and 31, *for* manganic *read* margaric.

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## ERRATUM.

| Page | Lines |
|---|---|
| 544 | 1 and 5 *for* Nitric *read* Nitrous. |

JOURNAL

OF

THE CHEMICAL SOCIETY.

## PAPERS READ BEFORE THE CHEMICAL SOCIETY.

### I.—*On the Action of Water and of various Saline Solutions on Copper.*

By THOMAS CARNELLEY, D.Sc., Demonstrator in the Chemical Laboratory of The Owens College.

HAVING lately been engaged in the working out of an accurate and delicate method for estimating colorimetrically very small quantities of copper, I thought it would be interesting to investigate fully the action of distilled water and of water holding various salts in solution on this metal. About the time I commenced the work my friend, Mr. Pattison Muir, published a paper on the same subject before the Manchester Literary and Philosophical Society (Proc., vol. xv, No. 3, p. 40), and had I not already obtained results differing from his, I should have discontinued working in this direction. The results obtained by Mr. Muir were, with one exception, negative, no copper being dissolved. He examined the action of distilled water, ammonium nitrate, potassium nitrate, ammonium sulphate, and mixtures of these salts, and the only liquid which exercised any solvent action upon the copper was that containing a large quantity of ammonium nitrate (0·408 gram per litre), and that only after 150 hours' contact with the copper, the amount of metal which then passed into solution being 3 mgrms. per litre. In my experiments, on the contrary, I have found that not only do solutions of all the salts tried, but also that distilled water itself dissolves a distinct amount of copper on standing in contact with the metal even for one hour only. The cause of this seeming discrepancy is owing to the fact that Mr. Muir did not expose a sufficient surface of copper to obtain an amount of the metal in solution large enough to be detected and estimated; for whereas the extent of

surface he exposed was only 0·042 sq. decm., the amount which I used was 1 sq. decm., or nearly 25 times as great, the quantity of water generally used with this amount of copper being 100 c.c.

Though the amount of copper exposed was comparatively large with respect to the volume of water, yet we may safely assume that the same solvent action takes place with smaller quantities, though to a proportionately less extent, and as copper exerts on the human system a very poisonous effect, it is important to know what solvent action different waters have on this metal, especially as copper vessels are so largely used for various culinary purposes, and as pipes and cisterns composed of it are not unfrequently employed for conveying and storing water intended for household use.

That most waters, on passing through copper pipes, &c., can take up a greater or less quantity of this metal into solution, has been shown by several chemists, among whom I may mention Reichart, who found (*Arch. Pharm.* [3], ii, 513) that water which took up, when freshly laid on in 1859 through copper pipes, 7·23 mgrms. of this metal per litre, took up 0·8 mgrm. per litre in 1872. Even this latter water gave a perceptibly green metallic soap. Although the quantity had diminished during the 13 years, yet at the end of that time a most objectionable amount of copper was still taken up. Again, Roux found (*Jour. Pharm.* [4], xiv, 104) that a water used for drinking in a certain village, and supposed to be the cause of an epidemic which had broken out there, contained a large amount of copper, and further examination showed that the presence of the metal in this water was due to the use of copper pumps and pipes.

Bergeron and Hôte have published a paper in the *Compt. rend.* (lxxx, 268) on the presence of copper in the animal organism. The kidneys and livers of fourteen human bodies were examined for copper with the following results:—In two individuals, aged 17, its presence could be proved only qualitatively; in eleven individuals, aged from 26 to 58, the quantities of copper ranged from 0·7 to 1·0 mgrm.; and in one individual of 78 years it amounted to 1·5 mgrm. The quantity of this metal contained in the systems of these persons appeared therefore to increase with the age. In the experiments the greatest care was taken not to introduce copper into the different liquids, the metal being determined by the intensity of colour produced by ammonia. These authors think that copper continually finds its way into the human body in consequence of the daily use of copper vessels, coins, &c.; and though the greater quantity of the metal is again eliminated from the system, yet a minute quantity is retained by the secretory organs, as the kidneys and liver.

The above cases will be sufficient to show, I think, the importance of the subject from a sanitary stand point; but there is also another

view which may be taken of this question, and that is with reference to the corrosive action which various waters have on the brass fittings of machinery and on brass taps, &c., which, with waters containing ammonical salts and chlorides, is in many cases considerable. In one of these, which has lately come under my notice, some brass water-gauge taps were so eaten away by one water, that they had to be renewed three times as often as was the case when another kind of water was employed. I intend shortly to publish some investigations on this part of the subject, when I hope to describe a method by which the corrosive action of various waters on brass, copper, and iron may be readily determined.

The following is a description of the method employed in the experiments given below for determining the action of water and of various saline solutions on metallic copper:—

Thin copper foil was cut into pieces of such a size that each exposed a surface of $\frac{1}{2}$ sq. decm. on each side or 1 sq. decm. in all; these were next cleaned by immersing them for some time in dilute nitric acid (1 to 6) and then thoroughly washing them with distilled water. In many cases it was not possible to remove all the stains entirely, especially those which had been produced during the passage of the metal through the rolling mill, as they appeared to extend right through the metal. The pieces were cleaned just before use and retained under water till they were transferred to the vessels in which the experiments were to be made. The liquids whose actions were to be tried were placed in beakers, and the requisite quantity of metal then dropped in, care being taken that the copper was entirely covered with the liquid during the whole of the experiment; the beakers were covered to protect them from dust and placed in a room apart from the laboratory, or exposed in a closet at the requisite temperature. After they had been exposed for a sufficient length of time, the copper was taken out and washed with distilled water, which was added to the rest of the liquid. In cases where a deposit had been formed, a few drops of nitric acid were added in order to dissolve the latter, and the liquid rendered as nearly neutral as possible with ammonia. The quantity of copper in the liquid was finally determined by means of the colorimetric method described by me in a paper read before the Manchester Literary and Philosophical Society (Proc., vol. xv, No. 2, Session 1875–6, p. 24, and *Chem. News*, vol. xxxii, p. 308).

I will now give an account of the results which I have obtained, dividing them into three heads. (A.) Action of distilled water. (B.) Action of solutions of single salts. (C.) Action of solutions of mixtures of salts.

### A. *Action of Distilled Water.*

The water employed was in all cases obtained by distilling Manchester town's water in glass retorts, its reaction being perfectly neutral.

Though with respect to the amount of copper dissolved by distilled water concordant results were not always obtained, yet I think they were as much so as could be expected from the nature of the experiment.

1. *Influence of the Time of Exposure.*—In each case 2 sq. decm. of copper were exposed in 100 c.c. of water at the ordinary temperature for various times. The following table shows the results thus obtained. Those experiments which were started at the same time are arranged in the same horizontal line, and this is the case throughout all the following tables. In all cases the quantity of copper dissolved is represented in milligrams.

TABLE I.

| No. of Experiment. | Time of Exposure in Hours. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1. | 2. | 3. | 4. | 6. | 24. | 48. | 54. | 72. |
| 1 | ·03 | ·05 | ·07 | ·07 | — | ·07 | — | — | — |
| 2 | — | — | — | — | ·22 | ·23 | ·23 | ·29 | ·32 |
| 3 | ·04 | — | ·07 | ·09 | ·09 | ·26 | ·15 | — | ·24 |
| 4 | — | — | — | — | — | ·27 | — | — | — |
| 5 | — | — | — | — | — | — | {·24 ·20} | — | — |
| 6 | — | — | — | — | — | — | ·21 | — | — |
| 7 | — | — | — | – | — | {·09 ·09} | — | — | — |
| Mean .. | ·035 | ·050 | ·070 | ·085 | ·155 | ·168 | ·210 | ·290 | ·280 |

From these numbers it appears that the quantity of copper dissolved increases with the time of exposure, but nothing like in the same ratio, the increase taking place very slowly.

2. *Influence of the amount of Copper exposed.*—In each of these experiments the quantity of copper given at the head of the respective columns of the following table was exposed in 100 c.c. of water for 48 hours at the ordinary temperature.

TABLE II.

| No. of Experiment. | Surface of Copper in Sq. Decimetres. | | | |
|---|---|---|---|---|
| | 1. | 2. | 4. | 6. |
| 1 | ·16 | {·24 ·20} | {·30 ·39} | ·50 |
| 2 | — | ·23 | — | — |
| 3 | — | — | — | ·49 |
| 4 | ·08 | ·21 | ·21 | ·34 |
| 5 | — | ·15 | — | — |
| 6 | ·08 | — | — | — |
| 7 | ·13 | — | — | — |
| Mean.... | ·11 | ·21 | ·30 | ·44 |

Here the action increases gradually with the extent of surface exposed, though it does not appear to bear any definite relation to the latter.

3. *Influence of the Quantity of Water.*—2 sq. decms. of copper were exposed for 48 hours at the ordinary temperature in the volumes of water shown in table III.

TABLE III.

| No. of Experiment. | Quantity of Water Present. | | |
|---|---|---|---|
| | 100 c.c. | 200 c.c. | 300 c.c. |
| 1 | {·24 ·20} | ·28 | ·29 |
| 2 | ·23 | — | — |
| 3 | ·21 | ·30 | ·26 |
| 4 | ·15 | — | — |
| Mean.... | ·21 | ·29 | ·28 |

The quantity of water present seems to have little or no effect on the total quantity of copper dissolved; if anything it slightly increases it: the amount taken up therefore per litre varies almost inversely as the volume of water present.

4. *Influence of the presence of Solder.*—As the joinings of many copper vessels and pipes are made with solder, it was considered worth while to try the influence of the latter when exposed together with copper to the action of water. Small pieces of solder of about

equal surface were used. The action of the water on the solder itself was not determined, but only that on the copper. At the end of the experiments small glistening metallic scales were usually found suspended in the liquid, these having been derived from the solder. The following table shows the results obtained:—

TABLE IV.

| No. of Experiment. | Copper only exposed. | Copper and Solder exposed. | Conditions under which the Experiments were carried out. |
|---|---|---|---|
| 1 | ·97 | ·05 | 2 sq. decm. copper exposed in 100 c.c. water for 48 hours at the ordinary temperature. |
| 2 | ·14 | ·08 | Ditto, at 90—100° C. |
| 3 | ·16, ·13, ·08 | ·05 | 1 sq. decm. copper exposed in 100 c.c. water for 48 hours at the ordinary temperature. |
| 4 | ·07 | ·07 | Ditto, at (90—100°) C. |
| Mean | ·116 | ·066 | |

The numbers given in the first experiment were obtained with copper which had been cleaned by washing with water only, and not by previous treatment with nitric acid; they are omitted in the average.

From this table it appears that the solder diminishes the solvent action of water on copper, but is in all probability attacked to a greater extent itself, by playing the part of the positive element in a copper-solder couple.

5. *Influence of Temperature.*—From the following table it is seen that the action of pure water on copper is less at (90°—100°) than at the ordinary temperature.

TABLE V.

| No. of Experiment. | At the Ordinary Temperature. | At (90°—100°) C. | Conditions of the Experiments. |
|---|---|---|---|
| 1 | ·24 | ·14 | 2 sq. decm. copper exposed in 100 c.c. water for 48 hours. |
| 2 | ·08 | ·05 | 2 sq. decm. copper exposed in 100 c.c. water for 24 hours. |

From the above five tables we may conclude, then, that the weight of copper dissolved by the action of distilled water alone is increased

by the time of exposure and by the extent of metallic surface exposed, and, on the other hand, is diminished by the presence of a more positive substance, as solder, and by rise of temperature, while the quantity of water in contact with a fixed amount of copper seems to have little or no effect.

The metal was always much discoloured after exposure *alone* at (90°—100°), while if solder were present it remained almost quite bright.

### B. *Action of Solutions of Single Salts.*

These solutions, with the exception of the alkaline carbonates, were all neutral, and the weights of the different salts are given in the anhydrous state. In the case of the more active salts the solutions were, especially when strong, coloured deep blue, while with the chlorides and ammonium sulphate deposits were found in the liquids subsequent to exposure; after removing the copper, these deposits were always dissolved in a few drops of nitric acid, and the liquid neutralised with ammonia as nearly as possible without producing a precipitate. In all cases the liquids, except of course the alkaline carbonates, were neutral after exposure, while in some cases the surface of the copper was very much stained and blackened.

1. *Relative Action of Different Salts.*—The weights of the various salts given in Table VI were dissolved in 100 c.c. of water and 1 sq. decm. of copper exposed in each for 48 hours. Those numbers marked

TABLE VI.

| Grams of Salt in Solution. | ·001. | ·01. | ·05. | ·50. | 5·00. |
|---|---|---|---|---|---|
| Potassium nitrate | ·13 | .07 | ·13 | ·14 | ·16 |
| Sodium „ | — | — | ·18* | — | ·19* |
| Calcium sulphate | — | — | ·09, ·11 * | — | — |
| Potassium „ | ·11 | ·09 | ·12 | ·16 | ·28 |
| Magnesium „ | — | — | ·16* | — | ·34* |
| Sodium carbonate | ·06, ·06 | .05, ·06 | ·11 | ·28, ·30, ·28, ·31 | 2·80 |
| Potassium „ | — | — | ·14* | — | 2·35* |
| Sodium chloride | ·08, ·07 | .04, ·07 | ·18, ·11 | 1·63 | 7·50* |
| Potassium „ | — | — | — | — | 8·17* |
| Ammonium sulphate | ·17 | ·17 | ·66 | 2·35 | 28·50* |
| „ nitrate | ·08 | ·19 | ·68 | 3·33 | 60·00* |
| „ chloride | — | — | ·92 | — | 158·75* |

with an asterisk in this table, and in the whole of those given in Table XI are not strictly comparable with the others, since they were obtained by using a different sample of copper, all the metal which had been employd to obtain the other numbers having become too badly stained to be satisfactorily cleaned. This second sample of copper was softer than the first, and appeared to be more easily acted on.

From the above table it appears, as far as the salts investigated are concerned, that, with the exception of the ammonium salts, the nature of the base has only a comparatively small effect, the action of the salt depending chiefly on the nature of its acid radical, and also that of these acid radicals the following is the order of action, beginning with that which has the least: nitrates, sulphates, carbonates, and chlorides.

The greatest action of all is exerted by the ammonium salts, which far exceeds that of any other.

In the case of ammonium chloride, which was the most active, small greenish-white pearly plates always separated out when the solution contained 5 grams of salt to 100 c.c. of water; the substance thus formed is probably an ammoniacal chloride of copper, which I intend to investigate more closely.

The four following tables show the influence which the various conditions mentioned in the case of distilled water have on the weight of copper dissolved by solutions of some of the above salts. Many of the numbers here given are the mean of four or five separate determinations, which agreed well among themselves, and much better than those obtained in the case of distilled water, with which the action appeared to some extent irregular under apparently identical conditions.

1. *Influence of Time of Exposure.*—1 sq. decm. of copper was exposed for the undermentioned times at the ordinary temperature in 100 c.c. of water containing 0·5 grm. of the salt in solution.

TABLE VII.

| Salt. | Time of Exposure in Hours. | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1. | 2. | 3. | 4. | 6. | 24. | 48. | 72. |
| Potassium nitrate .... | ·04 | ·04 | ·05 | ·07 | ·04 | ·17 | ·15 | ·20 |
| „ sulphate... | ·04 | ·06 | ·07 | ·07 | ·06 | ·13 | ·17 | ·16 |
| Sodium carbonate .... | ·03 | ·04 | ·06 | ·06 | ·09 | ·20 | ·29 | ·29 |
| „ chloride ..... | 15 | ·16 | ·24 | ·21 | ·41 | ·82 | 1·41 | 2·25 |
| Ammonium sulphate.. | ·32 | ·22 | ·20 | ·66 | 1·90 | 2·37 | 2·35 | 9·25 |
| „ nitrate... | ·26 | ·23 | ·56 | 1·55 | — | 2·28 | 3·33 | 12·00 |

2. *Influence of the Amount of Metallic Surface Exposed.*—The quantities of copper given in Table VIII were each exposed in 100 c.c. of water containing ·5 gram of the salt, for 24 hours at the ordinary temperature.

TABLE VIII.

| Salt. | Surface of Copper exposed in sq. decimetres. | | | | | | |
|---|---|---|---|---|---|---|---|
| | ¼. | ½. | 1. | 1½. | 2. | 4. | 6. |
| Potassium nitrate ..... | ·08 | ·11 | ·17 | ·18 | — | — | — |
| „ sulphate..... | ·05 | ·12 | ·13 | ·19 | — | — | — |
| Sodium carbonate ..... | ·09 | ·16 | ·20 | ·38 | — | — | — |
| „ chloride..... | ·30 | ·49 | ·82 | 1·22 | — | — | — |
| Ammonium sulphate..... | — | — | 2·37 | — | 4·30 | 4·75 | 4·50 |
| „ nitrate ..... | ·40 | — | 2·28 | 3·87 | — | — | — |

3. *Influence of the Quantity of Water.*—This will of course depend on whether the weight of salt dissolved in the water is constant in each case, or whether it is proportional to the quantity of water; and on this account the following table is divided into two parts, each referring to one of these two cases respectively.

In each experiment 1 sq. decm. of copper was exposed for 24 hours at the ordinary temperature in the undermentioned quantities of water, which in the first series of experiments (given in the division (*a*) of the table) always contained 0·5 gram of the salt in question whatever the quantity of water, while in the second series (given under (*b*)) the weight of salt was proportional to the volume of water.

TABLE IX.

| | (*a*). | | | | (*b*). | | | |
|---|---|---|---|---|---|---|---|---|
| Volume of water .. | 100 c.c. | 200 c.c. | 300 c.c. | 500 c c | 100 c.c. | 200 c.c. | 300 c.c. | 500 c.c. |
| Weight of salt dissolved ..... | ·5 grm. | ·5 grm. | ·5 grm. | ·5 grm. | ·5 grm. | 1·0 grm. | 1·5 grm. | 2·5 grms |
| Potassium nitrate .. | ·17 | ·25 | ·22 | ·14 | ·17 | ·20 | ·19 | ·18 |
| „ sulphate | ·13 | ·17 | ·14 | ·07 | ·13 | ·20 | ·21 | ·22 |
| Sodium carbonate .. | ·20 | ·17 | ·12 | ·14 | ·20 | ·18 | ·26 | ·34 |
| „ chloride ... | ·82 | ·60 | ·60 | ·40 | ·82 | ·87 | 1·07 | 1·26 |
| Ammonium sulphate | 2·37 | 3·50 | 1·35 | 1·09 | 2·37 | 2·70 | 2·95 | 3·13 |
| „ nitrate | 2·28 | 2·37 | 1 66 | 1·22 | 2·28 | 3·75 | 6·49 | 9·16 |

4. *Influence of Temperature.*—In each experiment 1 sq. decm. of copper was exposed for 24 hours in 100 c.c. of water containing 0·5 gram of the salt in solution at the temperatures shown in the following table.

TABLE X.

| Salt. | At the ordinary temperature. | At (90—100°) C. |
|---|---|---|
| Potassium nitrate | ·17 | ·11 |
| „ sulphate | ·13 | ·11 |
| Sodium carbonate | ·20 | ·74 |
| „ chloride | ·82 | 1·60 |
| Ammonium sulphate | 2·37 | 4·14 |
| „ nitrate | 2 28 | 1 68 |

When exposed at (90°—100°) the copper was always much discoloured, and in the case of sodium carbonate it became quite black, being covered with a black velvety-looking film.

From the results given in the above tables it is seen that the weight of copper dissolved by the solutions of the different salts increases with the time of exposure, and with the surface of metal exposed, and also with the quantity of water present, if the weight of salt in solution also increases in the same ratio; but if the quantity of salt remains fixed while the volume of water increases, the weight of copper dissolved at first slightly increases and then gradually decreases as more water is used. With regard to the influence of temperature, Table X shows that with three of the salts, viz., potassium nitrate, potassium sulphate, and ammonium nitrate, the action is diminished at (90°—100°), while with the other three it is considerably increased.

### C. *Action of Solutions of Mixtures of Salts.*

With regard to this point only a few determinations were made, the results of which are embodied in the following table.

In each case 1 sq. decm. of copper was exposed for 48 hours at the ordinary temperature in 100 c.c. of water containing a mixture of two salts which are bracketed together in the table, the weight of each present being shown in the second column.

TABLE XI.

| Salts. | Weight of Salt. Grams. | Copper dissolved. Mgrms. |
|---|---|---|
| Sodium chloride | 5·0 | 7·50 |
| Sodium chloride | 5·0 | 9·00 |
| Potassium nitrate | 5·0 | |
| Sodium chloride | 5·0 | 9·25 |
| Potassium nitrate | 5·0 | |

TABLE XI—*continued.*

| Salts. | Weight of Salt. Grams. | Copper dissolved. Mgrms. |
|---|---|---|
| Sodium chloride ..... | 5·0 | 10·75 |
| Potassium sulphate ..... | 5·0 | |
| Ammonium sulphate ..... | 5·0 | 28·50 |
| Ammonium sulphate..... | 5·0 | 30·00 |
| Potassium nitrate ..... | 5·0 | |
| Ditto ..... | 5·0 | 32·00 |
| | 5·0 | |
| Ditto ..... | 5·0 | 31·50 |
| | 1·0 | |
| Ammonium nitrate ..... | 5·0 | 60·00 |
| Ammonium nitrate ..... | 5·0 | 53·00 |
| Potassium nitrate ..... | 5·0 | |
| Ditto ..... | 5·0 | 60·00 |
| | 5·0 | |
| Ammonium chloride..... | 5·0 | 158·75 |
| Ammonium chloride..... | 5·0 | 121·60 |
| Sodium ,, ..... | 5·0 | |
| Ammonium chloride..... | 5·0 | 128·00 |
| Potassium nitrate ..... | 5·0 | |
| Ditto ..... | 5·0 | 140·00 (?) |
| | 1·0 | |
| Ditto ..... | 5·0 | 129·00 |
| | 0·5 | |
| Ditto ..... | 5·0 | 131·00 |
| | 0·1 | |
| Ditto ..... | 5·00 | 137·00 |
| | 0·05 | |
| Ammonium chloride..... | 5·0 | 150·00 |
| Potassium sulphate ..... | 2·5 | |
| Ditto ..... | 5·0 | 154·00 |
| | 1·0 | |
| Ditto ..... | 5·0 | 154·00 |
| | 0·5 | |

These numbers show that the action of sodium chloride is somewhat increased by the presence of potassium nitrate, and to a greater extent by that of potassium sulphate.

The action of ammonium sulphate is very slightly increased by the presence of potassium nitrate, while that of ammonium nitrate is not altered, or, if anything slightly diminished.

With respect to ammonium chloride, its action is diminished by sodium chloride, and to a less extent by potassium nitrate, and to a less extent still by potassium sulphate, the influence of these salts increasing with the weight of them dissolved.

One of the chief conclusions to be drawn from the above experiments and results is, that waters contaminated by sewage (and therefore, as a

rule, containing, compared with other waters, large quantities of ammoniacal salts and chlorides in solution) are not only bad for household purposes on account of their actual composition, but also because where copper pipes, vessels, &c., are used, they have a greater action on that metal; and also that, on account of this greater action on copper, they are less suitable for use in generating steam, &c., where brass taps and machinery fittings are exposed to their action.

## II.—*On certain Bismuth Compounds.* Part II.

By M. M. Pattison Muir, F.R.S.E., Assistant Lecturer on Chemistry, the Owens College, Manchester.

1. In a paper communicated to the Society (*J. Chem. Soc.*, Feb., 1876, p. 144), I have shown that by gently heating together powdered bismuth and bromine in a reversed retort, tribromide of bismuth sublimes in the form of golden-yellow scales. In carrying out this process I noticed that, after prolonged heating, there always remained a light yellow-coloured solid, which refused to sublime: this solid I regarded as tribromide, mixed probably with metallic bismuth. Being desirous of obtaining a further quantity of one of the products of the action of dry ammonia upon bismuth-tribromide, I prepared the tribromide, but did not wholly separate the sublimed from the unsublimed portion. On heating this supposed tribromide in a stream of ammonia, I found that but a very small portion of it was acted upon by the ammonia: it seemed probable, therefore, that the tribromide was largely mixed with some other compound, upon which, under the conditions of the experiment, ammonia gas was without action. I therefore heated a portion of the yellow substance containing tribromide of bismuth and the supposed new compound in a tube of hard glass, whereby the tribromide was volatilised and condensed on the cold part of the tube, while a greyish-yellow powder remained. This powder proved to be a new oxybromide of bismuth.

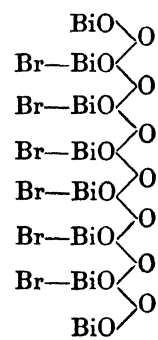
As I found that water was without action upon this oxybromide, while, as has been already shown, it decomposes bismuth tribromide, I shook up with water a quantity of the substance (from which the greater part of the tribromide had already been removed by heating) so long as the liquid became turbid. The residue was then dried at 100° and analysed. The analysis was carried out by placing a weighed quantity of the substance in a flask furnished with a funnel-tube, and with an exit-tube, which dipped into water contained in a beaker. By pouring moderately concentrated nitric acid through the funnel

tube, the salt was decomposed without heating; the very small quantity of evolved hydrobromic acid was absorbed by the water in the beaker. The following numbers were obtained:—

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| (1.) | 0·9765 | gram gave | 0·7675 | gram of | $Bi_2O_3$ | = 0·6888 | gram of | Bi. |
| (2.) | 0·339 | „ „ | 0·267 | „ | „ | = 0·239 | „ | „ |
| (3.) | 0·854 | „ „ | 0·6678 | „ | „ | = 0·5999 | „ | „ |
| (4.) | 0·630 | „ „ | 0·2965 | „ | AgBr and | 0·003 | „ | Ag. |
| (5.) | 1·3062 | „ „ | 0·6050 | „ | „ „ | 0·010 | „ | „ |

| | I. | II. | III. | IV. | V. | Mean. | Calculated for $Bi_8Br_6O_{15}$. |
|---|---|---|---|---|---|---|---|
| Bismuth.. | 70·51 | 70·50 | 70·19 | — | — | 70·34 | 70·00 |
| Bromine.. | — | — | — | 20·38 | 20·20 | 20·29 | 20·00 |
| Oxygen .. | | | | | | (diff.) 9·37 | 10·00 |

The most probable formula may be written $3\ Bi_2O_5.2BiBr_3$: or the substance may, perhaps, be looked on as an *oxybromide of bismuthyl*, thus:—




2. The new oxybromide is a grey lustrous powder, consisting of an aggregation of minute crystals: it is insoluble in water. Concentrated nitric acid quickly dissolves this compound, with evolution of hydrobromic acid: in dilute nitric acid it is soluble only after prolonged heating. Dilute hydrochloric acid dissolves it with tolerable ease. By dissolving a quantity of the oxybromide in hydrochloric acid containing a few drops of nitric acid, and pouring the solution into much water, a white, shining, crystalline precipitate was obtained, which contained bismuth and chlorine. An estimation of bismuth in this substance showed that it contained 80·42 per cent.: the oxychloride, $2BiCl_3.Bi_2O_3$, contains 79·39 per cent. of bismuth. If the solution of the oxybromide in hydrochloric acid be boiled down to a small bulk, and be then largely diluted with water, a white amorphous precipitate is formed, which is probably the oxychloride BiOCl.

The new oxybromide of bismuth is not changed by prolonged con-

tact with air; it is partly volatilised in greenish-white vapours when slightly heated over the blowpipe; the residue appears to consist of unchanged oxybromide. When heated with dry charcoal, the oxybromide is reduced, with formation of bismuth tribromide. The action of dry hydrogen upon this compound at a low red-heat brings about a change in the colour of the substance from grey to reddish-brown, and finally to black; the issuing hydrogen carries with it, mechanically, particles of a bismuth salt, inasmuch as if passed into water it causes the formation of a white precipitate containing bismuth and bromine —probably oxybromide, BiOBr. The reddish-brown substance produced in the above reaction was separated, and the quantity of bismuth in it was estimated: the amount found nearly coincided with that contained in the original oxybromide. The final product of the action of hydrogen upon this compound is metallic bismuth. Inasmuch as very considerable quantities of this oxybromide are always produced in preparing tribromide of bismuth by the method described in a previous paper, I have modified that method somewhat by conducting the operation in a reversed retort, through which a very gentle stream of dry carbon dioxide is passed. By this means a better yield of bismuth tribromide is obtained, but the process involves the expenditure of a larger amount of bromine.

3. In my former paper, when describing the action of dry ammonia gas upon tribromide of bismuth, I stated that an ash-grey substance remained in the boat in which the tribromide was heated. I have attempted to prepare this substance in quantity, but have not succeeded. *Very gentle* heating of tribromide of bismuth in a *slow* stream of ammonia appears to be the best method for forming this compound, but the quantity obtained is even then so very minute, that, after the expenditure of a large amount of tribromide, I have only been able to obtain less than 0·5 gram of the substance.

I give the following estimations of bromine and of bismuth, therefore, only as approximate numbers, and am not inclined to place very much value upon them :—

(1.) 0·1583 gram gave 0·1145 gram of $Bi_2O_3$ = 0·1028 gram Bi.
(2.) 0·1167 „ „ 0·1005 „ „ = 0·078 „ „
(3.) 0·1167 „ „ 0·040 „ Ag = 0·0296 „ Br.

| | Calculated for $BiN_2Br$. | Found. I. | II. | III. |
|---|---|---|---|---|
| Bismuth ..... | 66·04 | 65·89 | 66·84 | — |
| Bromine ..... | 25·16 | — | — | 25·36 |
| Nitrogen ..... | 8·80 | — | — | — |

If $BiN_2Br$ be the true formula for this body, it might be regarded as

two molecules of ammonia in which five hydrogen atoms are replaced by one bismuth, and the sixth by bromine, thus :—

$$\left.\begin{matrix} N \\ N \end{matrix}\right\} \begin{matrix} Bi^{v} \\ Br \end{matrix}$$

Or as a derivative of (hypothetical) bismuth pentabromide, $BiN_2^{iv}Br$.

4. In a paper published in the April number of the Society's Journal (1876, i, 483), I have described a process for the volumetric estimation of bismuth, founded upon Löwe's observations (*J. pr. Chem.* lxvii, 288) that chromate of bismuth is precipitated on the addition of potassium dichromate to a nearly neutral solution of bismuth nitrate. As, however, the exact composition of the bismuth chromate produced in the above reaction is still doubtful, I have undertaken a series of experiments with the view of determining the formula of this salt.

5. Löwe (*loc. cit.*) describes two bismuth chromates, to which he assigns the formulæ $3Bi_2O_3.2CrO_3$ and $Bi_2O_3.2CrO_3$ respectively: the former is produced by adding a solution of potassium chromate to a neutral solution of bismuth nitrate; the latter by digesting this salt with a small quantity of nitric acid, or by precipitating a neutral solution of the nitrate with excess of potassium dichromate.

6. I dissolved a quantity of metallic bismuth in nitric acid, boiled off the greater part of the acid, and added a solution of potassium chromate, whereupon a dense yellow precipitate was produced and quickly settled to the bottom of the vessel. This precipitate, when washed with boiling water, dried at 100°, and analysed, gave numbers agreeing with those required by the formula $Bi_2O_3.2CrO_3$ assigned by Löwe to this salt. A further quantity of a solution of bismuth nitrate prepared as already described was precipitated with an excess of potassium dichromate; the precipitate, when washed and dried at 100°, had likewise the composition expressed by the above formula. These results are in keeping with those of Löwe. Pearson (*Phil. Mag.*, [4], xi, 204) assigns the formula $Bi_2O_3.CrO_3$ to the salt obtained by precipitating bismuth nitrate with potassium dichromate, but taking Löwe's extended series of analyses in conjunction with my own, I cannot but greatly doubt the accuracy of Pearson's numbers.

I have not obtained the salt $3Bi_2O_3.2CrO_3$ described by Löwe, because the solution of bismuth nitrate with which I worked was always made distinctly acid by means of nitric acid.

7. Löwe mentions the fact that the yellow chromates of bismuth prepared by him are converted into a red salt or salts by boiling with caustic alkali; he does not appear to have inquired into the composition of this red substance. To a quantity of the freshly precipitated

salt obtained by adding potassium chromate to bismuth nitrate under the conditions already detailed, a few drops of nitric acid were added, and the whole was boiled for 3—4 hours: the yellow colour of the original chromate slowly changed to red, which became more and more brilliant in shade as the boiling continued. When no further change in the colour of the solid substance could be detected by continued boiling, the liquid was decanted, the salt was washed with boiling water until every trace of acid was removed, and the wash-water was no longer coloured; it was then dried at 100° and analysed.

| | | | | | | |
|---|---|---|---|---|---|---|
| 1. | 0·18024 gram | gave | 0·1484 | gram $Bi_2O_3$ | = 0·1331 | gram Bi. |
| 2. | 0·4506 | ,, | 0·3690 | ,, | = 0·3311 | ,, |
| 3. | 0·18024* | ,, | 0·150 | ,, | = 0·1346 | ,, |
| 4. | 0·18024 | ,, | 0·024 | gram $Cr_2O_3$ | = 0·0166 | gram Cr. |
| 5. | 0·4506 | ,, | 0·064 | ,, | = 0·0438 | ,, |
| 6. | 0·7032 | ,, | 0·091 | ,, | = 0·0623 | ,, |

| | I. | II. | III. | IV. | V. | VI. | Mean. | Calculated for $Bi_2O_3.CrO_3$. |
|---|---|---|---|---|---|---|---|---|
| Bismuth.... | 73·85 | 74·67 | 73·48 | — | — | — | 74·00 | 73·94 |
| Chromium.. | — | — | — | 9·21 | 9·64 | 8·84 | 9·23 | 9 15 |

8. On boiling the chromate obtained by precipitating bismuth nitrate with excess of potassium dichromate, with a very little nitric acid, it also was converted into a brilliantly red-coloured salt: this salt was washed, dried at 100°, and analysed.

| | | | | | | |
|---|---|---|---|---|---|---|
| 1. | 0·5976 gram | gave | 0·5025 | gram $Bi_2O_3$ | = 0·4509 | gram Bi. |
| 2. | 0·23905 | ,, | 0·1990 | ,, | = 0·1785 | ,, |
| 3. | 0·5976 | ,, | 0·085 | gram $Cr_2O_3$ | = 0·0582 | gram Cr. |
| 4. | 0·23905 | ,, | 0·0308 | ,, | = 0·0211 | ,, |

| | I. | II. | III. | IV. | Mean. | Calculated for $Bi_2O_3.CrO_3$. |
|---|---|---|---|---|---|---|
| Bismuth .... | 75·47 | 74·68 | — | — | 75·07 | 73·94 |
| Chromium .. | — | — | 9·74 | 8·82 | 9·28 | 9·15 |

9. The new chromate of bismuth is a vermillion-coloured salt, consisting of an aggregation of very minute microscopic needles; it is insoluble in water, but is easily dissolved by dilute hydrochloric acid; it is also soluble, although not so readily, in dilute nitric or sulphuric acid. The salt is partly dissolved by hot caustic soda-solution, and partly transformed into a yellow chromate, probably $Bi_2O_3.CrO_3$. This chromate is not changed by gentle heating over a Bunsen lamp, but when more strongly heated it is converted into a dark-brown substance, which is insoluble in water; but is readily dissolved by dilute hydrochloric acid, with formation of a very dark coloured liquid.

10. In order to determine the circumstances which principally condition the formation of the red from the yellow chromate, a quantity of the latter was allowed to remain in contact with a solution of potassium dichromate and a few drops of nitric acid for six weeks, at ordinary temperatures; a very small amount of red salt was produced, but the production soon ceased. By decanting the supernatant liquid, adding dichromate solution and a little acid, the production of red chromate of bismuth seemed to be slightly increased, but eventually only a very small percentage of the yellow was in this way converted into the red salt.

I found also that boiling the yellow chromate in contact with excess of potassium dichromate in a neutral solution brought about no change in the former salt, but that the presence of a small quantity of caustic potash or soda caused the formation, at a boiling temperature, of the red salt, although much more slowly and to a much smaller extent than was the case with nitric acid.

11. If this red chromate be boiled with a small quantity of concentrated nitric acid, it is partly dissolved and partly converted into a mass of small ruby-red crystals: by evaporating the solution a further quantity of the red crystals is obtained, and the mother-liquor from these, when poured into water, deposits a copious precipitate of a light yellow colour.

The ruby-red crystals appear, under the microscope, as monoclinic prisms; they are insoluble in water whether hot or cold; they are easily dissolved by dilute hydrochloric or nitric acid.

The ruby-red crystalline salt was dried at 100°, washed repeatedly with hot water, again dried at 100°, and analysed with the following results:—

1. 0·2555 gram gave 0·128 gram $Bi_2O_3$ = 0·1149 gram Bi.
2. 0·2555 ,, 0·126 ,, = 0·1122 ,,
3. 0·2555 ,, 0·088 gram $Cr_2O_3$ = 0·0602 gram Cr.
4. 0·2555 ,, 0·0875 ,, = 0·0599 ,,
5. 0·3242 gram lost 0·0045 on heating to 200°—250°.
6. 0·274 ,, 0·0040 ,, ,, ,,

| | I | II. | III. | IV. | V. | VI. | Mean. | Calculated for $Bi_2O_3.4CrO_3.H_2O$. |
|---|---|---|---|---|---|---|---|---|
| Bismuth.. | 44·97 | 43·82 | — | — | — | — | 44·39 | 44·73 |
| Chromium | — | — | 23·56 | 23·44 | — | — | 23·50 | 23·55 |
| Water.... | — | — | — | — | 1·39 | 1·64 | 1 52 | 2·03 |

The yellow precipitate obtained by pouring the mother-liquor from the red crystals into water, when washed and examined was found to

correspond in its general chemical behaviour with Löwe's yellow chromate, $Bi_2O_3.2CrO_3$: the same salt was obtained by dissolving the ruby-red salt in a little strong nitric acid and pouring the solution into water. The action of strong nitric acid upon the red chromate—$Bi_2O_3.CrO_3$—may very probably be represented thus:—

$$6(Bi_2O_3.CrO_3) + 8HNO_3 = Bi_2O_3.4CrO_3 + Bi_2O_3.2CrO_3 + 8(BiO)NO_3 + 4H_2O.$$

Strong hydrochloric acid dissolves the salt, $Bi_2O_3.4CrO_3$, with evolution of chlorine: on evaporating the solution to a very small bulk, a thick, dark red, semi-solid, non-crystalline mass is obtained, which on the addition of water yields a very light-yellow coloured flocculent precipitate, which is insoluble in hot water, but is easily dissolved by dilute acids, and which contains bismuth and chromium.

By prolonged boiling first with dilute nitric acid, then with water, $Bi_2O_3.4CrO_3$ is transformed into another light orange-coloured chromate, the exact composition of which I have not as yet ascertained.

When the ruby-red chromate is very gently heated over a Bunsen flame, it parts with water of crystallisation: at a somewhat higher temperature it undergoes decomposition, reddish fumes are given off, and a very dark green powder remains, which is with difficulty soluble in acids.

12. In one instance when boiling a quantity of the yellow chromate ($Bi_2O_32CrO_3$) with caustic soda, I found that the formation of red salt did not take place to any appreciable extent; I therefore removed the greater part of the alkali by washing, added nitric acid, and heated the liquid for some days at a temperature of about 60°, when I found that the yellow salt was converted into highly crystalline, shining, reddish-coloured needles. These crystals were thoroughly washed, dried at 100°, and analysed.

1. 0·2148 gram gave 0·1475 gram $Bi_2O_3$ = 0·1323 gram Bi.
2. 0·2148 „ 0·1495 „ = 0·1341 „
3. 0·2148 „ 0·049 gram $Cr_2O_3$ = 0·0336 gram Cr.
4. 0·2148 „ 0·050 „ = 0·0342 „
5. 0·2148 „ 0·051 „ = 0·0349 „
6. 0·2148 „ 0·052 „ = 0·0356 „
7. 0·3893 gram lost 0·0098 gram on heating.
8. 0·1695 „ 0·0045 „ „

| | I. | II. | III. | IV. | V. | VI. | VII. | VIII. |
|---|---|---|---|---|---|---|---|---|
| Bismuth.. | 61·59 | 62·43 | — | — | — | — | — | — |
| Chromium | — | — | 15·65 | 15·92 | 16·25 | 16·57 | — | — |
| Water.... | — | — | — | — | — | — | 2·52 | 2·66 |

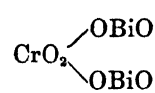
| | Mean. | Calculated for $Bi_2O_3.2CrO_3H_2O$. |
|---|---|---|
| Bismuth..... .. | 62·01 | 61·19 |
| Chromium..... | 16·09 | 15·21 |
| Water ..... | 2·59 | 2·62 |

13. This salt presents the appearance of brilliant orange-yellow crystalline needles belonging to the monoclinic system: the crystals appear of a canary-yellow colour when viewed under the microscope by reflected light, but orange-yellow when viewed by transmitted light: they do not undergo any change by heating to 150°: by gentle heating over a Bunsen lamp, they part with water of crystallisation, and become of a deeper orange colour.

When strongly heated, the orange-yellow crystals become perfectly black, but retain their crystalline form unaltered: at a higher temperature the black crystals fuse and are partly decomposed. This salt is insoluble in water even after protracted boiling; it is readily dissolved by dilute hydrochloric acid, less easily by dilute nitric acid. The black crystals which remain on heating the original salt are less soluble in acid than that salt, and their solution is of a darker and more green colour than that of the original salt.

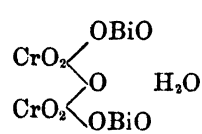
14. For the three chromates of bismuth described in the foregoing pages, and for Löwe's salt, I would propose the following names, which seem to me to express their composition with a tolerable degree of accuracy:—

*a*. The red chromate, $Bi_2O_3CrO_3$, may be represented by the formula—



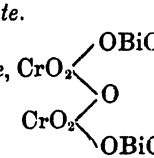
and may be called *bismuthyl chromate.*

*b*. The crystalline orange-yellow salt, $Bi_2O_3.2CrO_3H_2O$, may be represented by the formula—



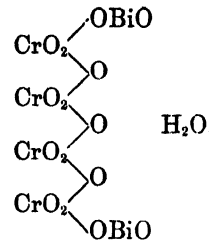
and may be called *monohydrated bismuthyl dichromate.*

*c*. Löwe's salt then becomes *bismuthyl dichromate*,



*d*. The ruby-red crystalline salt, $Bi_2O_3.4CrO_3.H_2O$, may be called

*monohydrated bismuthyl tetrachromate*, and may be represented by the formula—




I hope to be able to communicate to the Society, in a future paper, the results of further researches upon the chromates and other salts of bismuth.

## III.—COMMUNICATIONS FROM THE PATHOLOGICAL LABORATORY OF DR. THUDICHUM.

### No. I.—"*On Glycero-phosphoric Acid and its Salts, as obtained from the Phosphorised Constituents of the Brain.*"

By J. L. W. THUDICHUM and C. T. KINGZETT.

(1.) GLYCERO-PHOSPHORIC acid was first prepared synthetically by Pelouze from glycerin and phosphoric acid, by heating these bodies together at a somewhat high temperature. Soon after Pelouze had constructed the acid synthetically, Gobley obtained it from egg lecithine ($C_{42}H_{84}NPO_9$) by decomposing this substance with acids. Subsequently Lehmann observed its presence in diseased brain-matter, and for many years the source of it in the brain was considered, by inference rather than observation, to be the above named lecithin, while certain well defined principles contained in brain-matter, from which glycero-phosphoric acid is formed on chemolysis, were overlooked.

Quite recently one of us has discovered the body named *kephalin* ($C_{42}H_{79}NPO_{13}$) in brain-matter, and has further already published some account of its decomposition-products (see *Rep. Medical Off. Privy Council*, New Series, No. iii).

When kephalin is boiled for many hours with baryta-water, there are formed the insoluble barium salts of certain new fatty acids, and a solution containing one or two nitrogenous bases, and baric glycero-phosphate. It is to the acid obtained in this way, that the present research more especially refers.

(2.) *Glycero-phosphate of lead* may be prepared from the solution of baric glycero-phosphate just described, by precipitation with any soluble salt of lead, as for example, the chloride or acetate. In order to entirely remove glycero-phosphoric acid in this way from the solution, it is necessary to concentrate and neutralise the latter from time to time, on account of a slight solubility of the glycero-phosphate of lead.

Glycero-phosphate of lead prepared synthetically is granular and white, and remains so on drying, whereas when it is obtained from kephalin it dries to a hard, brittle, slightly coloured mass, even when chemically pure.

On ignition, the salt leaves a residue of pyrophosphate of lead, and this offers a ready means of ascertaining the purity of the preparation. Thus with a specimen of the salt prepared as described from kephalin, it was found that 0·911 gram left a residue of 0·744 gram $Pb_2P_2O_7$, while theory requires 0·7104 gram.

(3.) *Glycero-phosphate of calcium* (normal salt) may be prepared from the lead salt by decomposition with hydrosulphuric acid, and neutralisation of the filtrate with calcic carbonate.

This salt is but little soluble in a hot concentrated aqueous solution, from which it is consequently deposited.

A quantity of the lead salt, of which some analytical evidence has been given above, was converted into calcic salt, and the solution evaporated near the boiling point, when a white deposit of calcic glycero-phosphate occurred. This, when washed and dried, was analysed. 0·3400 gram after strong ignition with the aid of nitric acid, left a residue of 0·207 gram, equal to 60·8 per cent. $Ca_2P_2O_7$. Pure calcic glycero-phosphate should leave 60·5 per cent. pyro-phosphate.

Another sample of the calcium salt prepared as described gave the following figures on analysis :—

$$\left.\begin{array}{l} C = 13{\cdot}243 \\ H = 3{\cdot}421 \\ Ca = 19{\cdot}149 \\ P = 14{\cdot}841 \\ O = 49{\cdot}346 \end{array}\right\}\text{per cent.} \quad \left.\begin{array}{l} = 2{\cdot}3 \\ = 7{\cdot}1 \\ = 1{\cdot}0 \\ = 1{\cdot}0 \\ = 6{\cdot}4 \end{array}\right\}\text{atoms, taking Ca} = 1.$$

There is in this analysis a slight deficiency in the carbon, while it leaves no doubt that the formula of the salt is $C_3H_7CaPO_6$. A third preparation gave the following analysis :—

$$\left.\begin{array}{l} C = 16{\cdot}30 \\ H = 3{\cdot}47 \\ Ca = 18{\cdot}96 \\ P = 14{\cdot}69 \\ O = 46{\cdot}58 \end{array}\right\} = \text{per cent.} \quad \left.\begin{array}{l} = 2{\cdot}9 \\ = 7{\cdot}3 \\ = 1{\cdot}0 \\ = 1{\cdot}0 \\ = 6{\cdot}1 \end{array}\right\}\text{atoms,}$$

which fully confirms the above inferred composition of this salt.

(4.) *Acid Glycero-phosphate of Calcium.*—A solution of the calcium salt neutral to test-paper, becomes, on heating and at the same time as the normal salt separates, acid to test-paper; and if the mother-liquor is now precipitated with alcohol, there is produced, not the normal but the acid salt. A portion precipitated in this way by alcohol was white and granular. It was dried at 100° C.

0·827 gram left on ignition 0·478 gram residue = 57·80 per cent. Now the normal salt would have given, as we have seen, 60·5 per cent. residue. By this observation we were led to the theory of an acid salt of this construction, $C_3H_7CaPO_6,C_3H_9PO_6$, giving a total formula of $C_6H_{16}CaP_2O_{12}$, and it was probable that on ignition such a salt would leave a residue of half-saturated acid pyrophosphate $H_2CaP_2O_7$, losing only $C_6,H_{14},O_5$.

On this theory, the residue should have amounted to 56·54 per cent.; it did amount to 57·80 per cent.

The idea of the existence of an acid calcium salt is supported by a corresponding salt of glycero-sulphuric acid known to exist. Glycero-sulphuric acid is $C_3H_5(HSO_2)O_3$, and forms an acid salt $C_3H_4CaSO_5$, $C_3H_6SO_5$.

(5.) *Glycero-phosphate of barium* prepared from synthetically made acid and baric carbonate was white, and behaved, as regards its insolubility in, and consequent precipitation from hot aqueous solution, similarly to the calcic salt. But this property of separation of the salt on boiling the solution, seemed to be only transient, for after a solution had stood for 16 hours since it was so precipitated, no precipitation occurred on again boiling the solution, and ammonia produced a voluminous precipitate in the solution, apparently indicating that some degree of decomposition of the salt had occurred.

Some of the salt was prepared from the solution resulting from the decomposition of kephalin by baryta, by precipitation with alcohol. This was redissolved in water, and reprecipitated by alcohol several times; finally it was dissolved in water, and concentrated by evaporation on the water-bath, when a deposit occurred, rather grey in colour. This was isolated, dried by pressure between folds of paper, and over $H_2SO_4$ *in vacuo*, and finally at 100° C. At 110° it was not affected; it was now analysed.

| | | | | |
|---|---|---|---|---|
| C | = 11·46 | per cent. | = 2·0 | atoms, leading to a formula of $C_3H_7BaPO_6$. |
| H | = 2·44 | | = 7·4 | |
| Ba | = 45·15 | | = 1·0 | |
| P | = 10·21 | | = 1·0 | |
| O | = 30·74 | | = 5·8 | |

Another specimen of baric glycero-phosphate was prepared much in the same way, but with one difference, that whereas the one, the

analysis of which has just been given, was separated from water by boiling, the one now to be described was precipitated from aqueous solution by alcohol, with which it was also washed. On isolation the precipitate contracted, became horny, transparent, and finally fused to a thick liquid. It eventually dried to a brittle mass. On analysis it gave—

$$\left.\begin{array}{l} C = 12{\cdot}611 \\ H = 2{\cdot}933 \\ Ba = 40{\cdot}950 \\ P = 9{\cdot}266 \\ O = 34{\cdot}240 \end{array}\right\} \text{per cent., leading to a formula of } C_3H_7BaPO_6,H_2O.$$

These observations led us to the surmise that the baric salt as precipitated by alcohol was a true alcoholate. The truth of this hypothesis was proved by the experiments now to be described.

(6.) *The Alcoholo-hydrated Baric Glycero-phosphate*.—A quantity of baric glycero-phosphate, as prepared by the chemolysis of kephalin with baryta, was precipitated by alcohol, and the precipitate washed with alcohol, after which it was exposed to the air, when it lost alcohol, became brown and somewhat brittle round the edges, and began to fuse. At this stage it was again dissolved in the minimum amount of cold water (very soluble), and the solution reprecipitated by absolute alcohol. The precipitate so prepared was isolated, allowed to drain, and a portion examined as follows:—

When thoroughly drained, a small quantity was pressed in a vice between folds of blotting-paper, until it became pulverulent. It was now heated in an air-bath at 100° C., until it was approximately dry. In this way 0·7354 gram lost 0·2376 gram, and became 0·4978 gram, corresponding to a loss of 32·30 per cent. The residue of this operation, when burnt, left a residue weighing 0·3064 gram, equal to 61·5 per cent.

Pure normal baric glycero-phosphate leaves on ignition 72·96 per cent. residue, while the hypothetical acid salt of formula $C_3H_7BaPO_6$, $C_3H_9PO_6$, might presumably leave under such conditions 65·3 per cent. of $H_2BaP_2O_7$.

A salt of the formula $\left.\begin{array}{l} C_3H_7BaPO_6 \\ C_3H_9 \quad PO_6 \end{array}\right\} H_2O$ would leave on ignition 62·9 per cent. $H_2BaP_2O_7$. After this preliminary experiment, the whole precipitate obtained by alcohol, and amounting to 71 grams, was dried by pressure between folds of paper, until it was quite pulverulent, then placed in 200 c.c. water, in which the substance first of all set like glue, but after 48 hours had not entirely dissolved.

An addition, however, of 100 c.c. more water gave a perfect reddish-brown solution, which was now subjected to distillation, and the

alcohol contained in the first 150 c.c. distillate determined. It was thus shown that in the 71 grams of glycero-phosphate, so dry that it could be powdered, there were 14·84 grams of absolute alcohol, or 20·9 per cent.

We abstain from giving any formula for this alcoholo-hydrate of baric glycero-phosphate. The general analytical results show—

| | | |
|---|---|---|
| Absolute ethylic alcohol..... | 20·9 | |
| Water ..... | 11·4 | |
| Total volatile at 100° C. .. | 32·3 | 32·3 |
| Residue of baric phosphate .... | 41·6 | (form undetermined.) |
| Volatile at red heat..... | 26·1 | |
| Total glycero-phosphate of Ba.. | 67·7 | 67·7 |
| | | 100·0 |

There are probably at least three molecules of alcohol and six of water combined with one molecule of acid glycero-phosphate in this compound.

The residue, from which the alcohol had been distilled, was concentrated by evaporation on a water-bath, when it deposited grey granular matter, which on analysis was found to be normal glycero-phosphate of barium, $C_3H_7BaPO_6$.

The mother-liquor obtained after the separation of the normal baric salt just alluded to, was again precipitated by absolute alcohol. The precipitate was dried by pressure between folds of paper until it was pulverulent. It now weighed 63 grams, and was dissolved in 300 c.c. water, and the solution distilled to one-half. On estimation of the alcohol, it was found that the salt had contained 15·5 per cent. absolute alcohol.

Finally the residual solution of barium glycero-phosphate was transformed into lead salt, and the lead salt into calcium salt. That portion of the calcium salt which was deposited from a boiling solution was found to be normal. From the mother-liquor, which grew acid, a salt was precipitated by alcohol, which, from a determination of the residue left on combustion of a portion of it, seemed to be the acid salt of calcium.

(7.) The salts of kryptophanic acid (from urine) and kreatylic acid (from flesh) present characters which recall those above attributed to glycero-phosphate of barium. Thus the copper salt of kryptophanic acid when precipitated by alcohol behaves like the glycero-phosphate

of barium already described, yielding, on distillation with water, alcohol.

The following alcoholates are known: $ZnCl_2,2C_2H_6O$; $CaCl_2,4C_2H_6O$; $Mg(NO_3)_2,6C_2H_6O$; &c.

Glycero-phosphate of barium not only seems to be the only organic compound which is known to form alcoholates, but it is in so far unique, as it is an *alcoholate* and a *hydrate* at the same time.

The differences observed in the relative amounts of alcohol and water may be caused by the different proportions of these bodies which are present at the moment of precipitation. If several alcoholo-hydrates are producible, the method of preparation makes it unavoidable that a mixture of these should be produced. But even if this were not the case, and if there were only one type of alcoholo-hydrate, the varying amounts of alcohol in different precipitations would compel us to assume that alcohol and water may substitute each other in indefinite proportions, as isomorphous compounds do in mixed crystals.

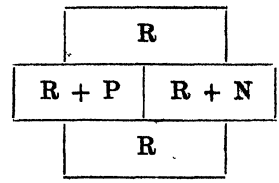
(8.) It is to be remarked that during the elementary analyses of the salts of glycero-phosphoric acid, some difficulty is experienced in burning the whole of the carbon: hence the results obtained are generally rather low as regards that element. When glycerin and phosphoric acid are heated together, even for a long time, only a small portion of both is transformed into glycero-phosphoric acid; it may be that the acid is constantly formed and again decomposed. And this idea is supported by the unstable character of the acid and its soluble salts.

The insoluble lead salt is very stable; next comes the calcium salt, then the barium salt.

Other salts, such as those of silver and copper, seem to decompose at every stage of their production, so that although voluminous at first, they fall away to almost nothing during attempts at their purification.

During all transformations or concentrations of solutions, considerable quantities of the acid are decomposed, and the relative phosphates and glycerine are formed.

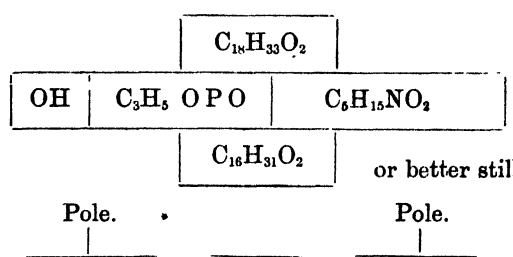
(9.) We now know three classes of phosphorised bodies in the brain, which contain glycero-phosphoric acid as a proximate nucleus. These are the kephalins, myelins, and lecithins. Of the constitution of these, one of us has given a diagram (in the research already alluded to) to show that they contain four classes of radicles each, which give rise to four different poles of combining power; the acid pole, the alkaloïdal pole, and two substitution-poles.



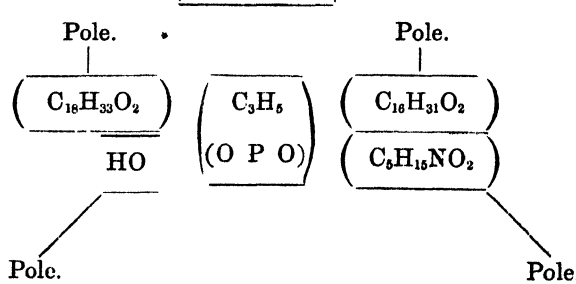

The acid pole, feebly developed as it is, seems to be mainly the result of the survival of one of the hydroxyls of the phosphoric acid radicle in the larger radicle of glycero-phosphoryl. The fatty acid radicles seem to occupy the places of the two hydroxyls of the glycerin left unoccupied by the phosphoryl; so that there is only one dynamicity left to which the nitrogenised nucleus (neurine or oxy-neurine, or choline) can be fastened, and this is the second hydroxyl of phosphoryl.

$$C_3H_5\left\{\begin{array}{l}OH.\\OH.\\OPO(OH)_2\end{array}\right. = \begin{array}{c}C_3H_9PO_6\\\text{Glycero-phosphoric acid.}\end{array}$$

$$C_3H_5\left\{\begin{array}{l}C_{18}H_{33}O_2\\C_{16}H_{31}O_2\\OPO\left\{\begin{array}{l}C_5H_{15}NO_2\\OH\end{array}\right.\end{array}\right. = \begin{array}{c}C_{42}H_{85}NPO_9\\\text{Lecithin.}\end{array}$$




or better still,




These formulæ explain the circumstance that the first observers of lecithin (Gobley and Diaconow) believed it to be a *salt-like* body.

# IV.—COMMUNICATIONS FROM THE PATHOLOGICAL LABORATORY OF DR. THUDICHUM.

## II. *On some Reactions of Biliverdin.*

By J. L. W. Thudichum, M.D.

In the following experiments a quantity of biliverdin was used, which had been prepared from bilirubin by Heintz's process, and on analysis had yielded the formula $C_8H_9NO_2$.

1. *Monobrominated Biliverdin.*—A quantity of finely powdered biliverdin, which when quite dry at 100° weighed 0·8064 gram, was treated in a Liebig's drying apparatus with dry bromine vapour mixed with dry air. It absorbed the bromine and became perfectly black. When the action of bromine had been allowed to complete itself during many hours, at the ordinary temperature, the excess of bromine was displaced by dry air. The product now weighed 2·3684 grams, or almost threefold the weight of the original biliverdin. The apparatus was now heated to 100° and dry air passed over the product for many hours. A little bromine and much hydrobromic acid escaped, and after the passing of more than two hundred litres of air (measured by the displacement of the water in the aspirator) the apparatus became of constant weight, and the substance lost mere vestiges of HBr. It now weighed 1·22236 gram. The equation

$$C_8H_9NO_2 + Br_2 = HBr + C_8H_8BrNO_2,$$

requires that 151 parts biliverdin should become 230 parts of brominated substitution-product, and therefore the 0·8064 biliverdin should have increased to 1·2282, equal to an addition of 0·4218 gram of bromine. This hypothesis is therefore very nearly satisfied by the experiment.

The new product is a perfectly black powder, insoluble in ether, very little soluble in alcohol; soluble in oil of vitriol, precipitated from this by dilution with water; the solution has a feeble purplish tint; soluble in caustic soda, precipitated from this in brown flakes by acetic acid. From the aspect of the reaction it is probable that the substance cannot be dissolved in either sulphuric acid or soda without change.

*Analysis.—a.* 0·0282 gram burned with copper oxide in vacuo yielded a mixture of gas which after the necessary corrections amounted to 23·78 c.c. Of this 22·4 c.c. were $CO_2$, and 1·38 were N. This is equal to 42·58 per cent. C., and 6·12 per cent. N. The relation of C : N is therefore = 8·1 : 1·0.

*b.* 0·1920 gram ignited in a glass tube with soda and nitre, &c., gave 0·1613 AgBr, equal to 35·72 per cent. Br.

*c.* A combustion with lead chromate in a very long tube yielded quantities which showed that the quotient of carbon by its atomic weight was to that of hydrogen as 3·22 to 3·179, or, in atoms, very nearly 8 : 8. These analyses, therefore, confirm the presumption derivable from the synthetical genesis of the product, namely, that it is $C_8H_8BrNO_2$. Theory requires 41·73 per cent. C; 3·47 per cent. H; 34·73 per cent. Br; 6·08 per cent. N; leaving for O 13·99 per cent.

This reaction, therefore, confirms the formula which (in consequence of my researches communicated in the 10th Report of the Medical Officer of the Privy Council, 1867, p. 240 to 251; also *Jour. pr. Chem.*, 104 (1868), 4, *et seq.*, and *Proc. Roy. Soc.*, xvi, 217) I have attributed to biliverdin, namely, $C_8H_9NO_2$. Incidentally the reaction by which bilirubin is transformed into biliverdin is also confirmed, and some additional light is thrown on the process:

$$C_9H_9NO_2 + O_2 = C_8H_9NO_2 + CO_2.$$

Bilirubin (as I have shown in a paper printed in the *Chem. Soc. J.*, May, 1875, p. 389) when treated with dry bromine vapour, yields up two atoms of hydrogen, and assumes two atoms of Br in their place:

$$C_9H_9NO_2 + Br_4 = 2HBr + C_9H_7Br_2NO_2.$$

This reaction I have confirmed by several new preparations and their elementary analyses (see my "Open Letter to the Imperial Academy at Vienna," &c., *Chemical News*, April 15 and 22, 1876). It is therefore clear that bilirubin, when passing into biliverdin, not only loses an atom of carbon, but also undergoes a change regarding the manner in which one of its atoms of hydrogen is bound, so that this hydrogen-atom, though capable of being replaced in bilirubin, is no longer replaceable by Br in biliverdin.

2. *Hydrobiliverdin.*—A quantity of biliverdin was dissolved in caustic soda and water, and some sodium-amalgam added. The mixture was repeatedly agitated. On the third day the solution, at first greenish, was brownish-red. Hydrochloric acid now gave a brown deposit which was collected on a filter and edulcorated with water. The filtrates were coloured reddish, and seemed to contain a side product, soluble in dilute HCl. The precipitate was treated with alcohol, and dissolved to a great extent, but a portion remained insoluble in even boiling alcohol, and ultimately formed a black powder. The alcoholic solution contained, however, the bulk of the new product.

*Spectral Phenomena of the Alcoholic Solution of Hydrobiliverdin.*—The concentrated dark-brown solution, with Drummond's light, trans-

mits red only. On greater dilution, all red, yellow, and some green rays pass; green is shaded Again more diluted, a separate feeble absorption-band appears at the junction of green and blue, overlying the line F equilaterally. This spectrum is, therefore, not identical with that of hydrobilirubin (see *Journ. Chem. Soc.*, May, 1875, 389, spectrum 8), in which the absorption-band fills the space between the lines E and F, overlapping them both, and is of unsymmetrical intensity, its greatest intensity being about one-third nearer to E than F. This experiment thus leads to a presumption that hydrobiliverdin and hydrobilirubin, though similar in external appearance and some properties, are not, as has been alleged, identical.

The alcoholic solution of hydrobiliverdin is precipitated by water. Ammoniacal solution of zinc chloride added to this dissolves all, and the solution fluoresces feebly greenish-brown in sunlight only; the fluorescence appears to be homochromatic.

## V.—*Note on the occurrence of Benzene in Rosin Light Oils.*

By Watson Smith, F.C.S.

In refining rosin obtained as a bye-product in the distillation of oil of turpentine (from crude turpentine), the dark-coloured crude rosin is placed in iron stills and superheated steam passed through the mass, the distilled rosin being deposited in a series of condensers. A quantity of light oils also passes over. The distillation is thus partially a destructive distillation. These light oils have formed the subject of a few experiments at different times.

In the year 1867, having occasion to examine the above-mentioned oils, I found that they contained a large proportion of *benzene*, together with products boiling below 80° C. This sample began to boil at 50°, and a large proportion of it passed over below 100°. This portion was carefully fractionated, and a considerable amount of product obtained, boiling constantly between 80° and 85°. It possessed all the properties of benzene, but appeared still to be slightly contaminated by turpentine-products, so that on treating it with fuming nitric acid, though the nitro-benzene was easily obtained, yet this product when tasted was found to possess, at first for an instant, the characteristic sweet taste of nitro-benzene, rapidly succeeded, however, by a most disagreeable acrid taste.

Since the time above mentioned the plant in the works whence the above sample was obtained, has undergone considerable alteration, the effect of this alteration being a considerably higher temperature used

in the rosin distillation in order to get a larger yield of rosin oils. Last year (1875) I made a further examination of this rosin spirit, and procured a sample of the first gallon of rectified spirit coming over from the "rectifier." It was perfectly clear and transparent, but of a faint yellow tint, deepening on exposure and keeping. 200 c.c. were placed in a flask and fractionally distilled, with the following results:—

*Liquid began to boil at* 109° C., *and the Distillate to drop in the Receiver at* 116° C.

| Temperature. | Vol. c.c. | Per cent. | |
|---|---|---|---|
| Below 120° | 7 | 3·5 | |
| „ 130 | 50 | 25·0 | ....Redistilled this fraction: It began to boil at 108° C., and the larger bulk of it came over below 117°. Smelled strongly of toluene, and readily yielded nitrotoluene with nitric acid. This was, however, contaminated with small quantities of turpentine products. |
| „ 140 | 44 | 22·0 | |
| „ 150 | 36 | 18·0 | |
| „ 160 | 28 | 14·0 | |
| „ 170 | 22 | 11·0 | |
| „ 180 | 8 | 4·0 | |
| „ 190 | 4 | 2·0 | |
| | | 99·5 | |

It would appear that the effect of using a comparatively low temperature in distilling the rosin with superheated steam, results in the yield of light oils containing a considerable proportion of benzene as a constituent, together with bodies boiling below 80°. That when higher temperatures are used, no benzene is obtained, or but traces, and toluene makes its appearance as the lowest-boiling member.

## VI.—*A new method for preparing the Hydrocarbons, "Diphenyl" and "Iso-dinaphthyl," and on the action, at a high temperature, of Metallic Chlorides upon certain Hydrocarbons.*

By Watson Smith, F.C.S.

### *Benzene and Antimony Trichloride.*

The mixed vapours of benzene and antimony trichloride were passed through a red-hot tube, when the following equation was realised:—

$$6C_6H_6 + 2SbCl_3 = 3\left|\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right. + 6HCl + Sb_2$$

The distillation was repeated several times. It was found that though the yield was greatly increased by this method above that obtained with benzene alone, yet that it was not as large as could be desired. The diphenyl was separated from the mixture of diphenyl, metallic antimony, and excess of antimony chloride by treatment with hydrochloric acid, and finally distilling with water, in the vapour of which the hydrocarbon is carried over. The experiment was now repeated with *tetrachloride of tin.*

*Benzene and Tin Tetrachloride.*

On passing the mixed vapours of these bodies through a red-hot tube filled with pumice-stone fragments, hydrochloric acid gas was copiously evolved, and the following equations were realised, both metallic tin and stannous chloride being reduced and found in the receiver :—

The mixed result is what is obtained

$$(1)\ 4C_6H_6 + SnCl_4 = 2\left|\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right. + 4HCl + Sn$$

$$(2)\ 4C_6H_6 + 2SnCl_4 = 2\left|\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right. + 4HCl + 2SnCl_2$$

By this method diphenyl is formed in large quantity, being found in the receiver in solid cakes, consisting of a mixture of diphenyl with some stannous chloride. It is undoubtedly the simplest and quickest method for procuring diphenyl in quantity.

*Toluene and Antimony Trichloride.*

Large volumes of hydrochloric acid evolved and much metallic antimony reduced. However, a tarry, oily mass was obtained, which yielded on distillation no stilbene, but at 270° a red oil smelling like burnt cheese; at from 280°—300° another oil, with a still ranker and more disagreeable odour, and at 350° or thereabouts a thick gummy oil, which crystallised, forming a striated mass of crystals. I am experimenting further in this derection.

*Naphthalene and Antimony Trichloride through a red-hot Tube.*

Considerable quantities of hydrochloric acid were evolved, metallic antimony reduced, and a largely increased yield of iso-dinaphthyl obtained. This is shown as follows :—

| | Per cent. |
|---|---|
| *Naphthalene alone used:* After eight distillations through red-hot tube, crude substance obtained ..... | = 17·23 |
| *Naphthalene and Antimony Trichloride:* After three distillations through red-hot tube, crude substance obtained ..... | = 48·5 |
| (After distilling to purify. Yellow crystalline substance partially purified ..... | = 31·4) |

In purifying the crude substance by triturating and washing with petroleum-spirit, a yellow substance is dissolved communicating a red tint to the spirit; from this solution crystals in wart-like masses gradually separate. This substance I shall now endeavour to isolate.

*Naphthalene and Tin Tetrachloride.*

The results of this experiment were hydrochloric acid gas, together with a considerable separation of carbon, metallic tin, and stannous chloride, and the formation of chlorinated substitution-products of naphthalene, and of a considerable amount of iso-dinaphthyl. It was found, however, that, owing to the frequent stopping up of the tube with reduced carbon, and continual danger of explosions, the method with antimony trichloride is much to be preferred, as it is quite easy of performance and presents neither of the above disadvantages.

In the above reactions it would appear that, in the *first case*, the following equation is realised:—

$$6C_{10}H_8 + 2SbCl_3 = 3\left|\begin{matrix}C_{10}H_7\\C_{10}H_7\end{matrix}\right. + 6HCl + Sb_2;$$

*in the second*—

$$\left\{\begin{array}{l} 4C_{10}H_8 + SnCl_4 = 2\left|\begin{matrix}C_{10}H_7\\C_{10}H_7\end{matrix}\right. + 4HCl + Sn. \\ \\ \text{and } 4C_{10}H_8 + 2SnCl_4 = 2\left|\begin{matrix}C_{10}H_7\\C_{10}H_7\end{matrix}\right. + 4HCl + 2SnCl_2. \end{array}\right.$$

Of course these equations represent only approximately what actually and totally takes place, other bodies being formed in small quantity.

The melting point and boiling point of the substance obtained in both the reactions named agreed with those of iso-dinaphthyl. A combustion was also made and gave the following results:—

| | Found. | Calculated for $C_{10}H_7$ \| $C_{10}H_7$ |
|---|---|---|
| Carbon..... | 93·97 | 94·48 |
| Hydrogen ..... | 5·50 | 5·52 |
| | 99·47 | 100·00 |

*Melting Point* = 186° *to* 187°.

This I find is also the melting point of iso-dinaphthyl, prepared from naphthaline alone, and the number I formerly gave (204°) is erroneous, having been obtained by too rough a method. The corrected melting point is therefore 187°. I have also discovered a new solvent for iso-dinaphthyl, viz., glacial acetic acid, from which the hydrocarbon separates on cooling in most beautiful and perfect rhomboïdal plates, exhibiting a delicate blue fluorescence.

I cannot forget to thank Prof. Merz, of Zürich University, for his kind assistance in this investigation.

# ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

## General and Physical Chemistry.

**Spectroscopical Notes.** By J. NORMAN LOCKYER (Pogg. Ann., clv, 136—146).

I. *On the Evidence of Variation in the Molecular Structure of Vapours.*—The author has made researches leading to the inference that a mass of elemental matter becomes continually broken up under the influence of an increasing temperature (or electrical action).

Solid bodies produce continuous spectra; vapours, produced by the high-tension spark, give line spectra.

From the fact that a continuous spectrum may be, and in fact is produced by chemical compounds, whereas compounds known as such become by the high-tension spark decomposed into their elements, the author assumes that an element in the solid state is a more complex mass than the element in a state of vapour, its spectrum being the same as that of a mass known to be more complex.

Cases are cited in which intermediate stages between these two extremes can be produced by the spectroscope. To take the first example, a variation in the spectra is produced on passing from the induced current with the jar to the spark without the jar, to the voltaic arc, or to the highest temperature produced by combustion, and this spectrum of elements in the state of vapour coincides with that produced by vapours, the compound nature of which is unquestioned. If therefore the various spectra referred to be really the result of different molecular aggregations, they will form a series passing from the more simple to the more complex.

The author gives a few instances of the passage of spectra from one stage to another.

II. *On the Molecular Structure of Vapours in Connection with their Densities.*—The author has attempted to determine whether vapours of elements below the highest temperatures are really homogeneous, and whether the vapours of different chemical elements, at the same temperature, are all in a similar molecular condition; this note contains the preliminary results of his researches, from which he concludes that, if similar spectra be taken as indicating similar molecular conditions, then the vapours, the densities of which have been determined, have not been in the same molecular condition among themselves; also that each vapour is non-homogeneous for a considerable interval of time, the interval being increased as the temperature becomes reduced. (From the *Proceed. of the Roy. Soc.*, 1874.)

H. H. B. S.

## New Lines in the Spectrum of Calcium.

By J. NORMAN LOCKYER (Compt. rend., lxxxii, 665).

IF calcium chloride be dissociated only slightly, the calcium line obtained is that one which is in the blue of the spectrum; as the amount of the dissociation increases, that line becomes more brilliant, and the spectrum of the chloride gradually disappears.

If the electric arc be employed, the blue line is extremely well developed, and at the same time two new lines, corresponding with the lines H in the solar spectrum, become visible. It is remarkable that the ray in the blue is broader and much more brilliant than those in the violet when the electric arc of a 30-cell Grove's battery is used, whereas in the solar spectrum the rays in the violet are the broadest in the whole of the spectrum, and the blue line is represented at best very feebly. Possibly between the temperatures which we can produce, and that of the sun, there is a difference which, as regards the spectrum of calcium, is the same as the different temperatures we can produce are for the chloride of calcium.

By the employment of batteries and coils of varying strength, it was possible to obtain a spectrum in which only the blue, or only the violet rays were visible, and which was verified by photographing the spectra so obtained. By varying the surface of the battery, a spectrum was obtained resembling the absorption-spectrum of calcium in the sun.

The author then questions whether the phenomena do not indicate a true dissociation of calcium itself, and he points out that the question can only be solved by photographing the calcium rays in the spectra of different stars. Prof. Stokes does not consider the evidence in favour of the dissociation of calcium as perfect, and he suggests as an explanation of the observed facts, that possibly with an increase of temperature the more refrangible lines increase in brilliancy at the expense of the less refrangible, although it was pointed out to him that such a law does not hold good in other cases, for instance, in the case of hydrogen, where an increase of temperature increases the intensity of the red line C of hydrogen.

C. H. P.

## New Electro-spectrum Tube.

By B. DELACHANAL and A. MERMET (Bull. Soc. Chim. [2], xxv, 194).

THIS instrument consists of a tube 11 cm. high, and 1·5 cm. diameter, closed at the lower end, through which passes a platinum electrode; into the open end of the tube fits a cork, through which passes a glass capillary tube, carrying a platinum wire, which is the other electrode. The important part of the apparatus is a short capillary tube slightly conical, which caps the lower electrode, and terminates about 0·5 cm. above it. To work the instrument, the liquid to be examined is poured into the tube to such a height, that only about half of the lower electrode is immersed; capillary action determines its ascent to the top of the tube surrounding the lower electrode, and upon passing the electric current, the illumination is produced, which can be observed for a long time without intermission.

The results of some experiments with the apparatus are recorded, one being the detection of gallium and indium in commercial zinc, which it is estimated contains about $\frac{1}{5,000,000}$ of the former, and $\frac{1}{500,000}$ of the latter metal.

C. H. P.

## Experimental Contributions to the Theory of Electrolysis.

By ALFRED TRIBE (Proc. Roy. Soc., 1876).

AFTER a short review of the history of the theory of electrolysis, the author continues:—If the condition of an electrolyte just prior to and in the act of decomposition be in accordance with the views of Grotthus and Faraday, an electrolyte may be regarded as a *di-electric*, whose molecules are possessed of the power of mutually exchanging their constituents during discharge. This view, jointly with some supposed points of resemblance between magnetic and electrolytic bodies, led to the following experiments:—

I. A piece of thin copper wire 1 inch long was hung lengthwise between platinum electrodes in a 5 per cent. solution of K.Cl. Hydrogen was at once given off from the end facing the positive pole, the other end being corroded.

II. Four silver strips $\frac{1}{2}$ inch long were suspended in a line between the electrodes in a 5 per cent. solution of copper sulphate mixed with a little potassium chloride. Clouds of silver chloride formed upon the ends facing the negative pole, and copper was found deposited upon the other ends. These effects are referred to electric induction.

III—IV. The action upon each of a series of 12 strips was found to be equal when the electrodes stretched quite across the ends of the trough.

V—VI. Determinations of the amount of copper deposited upon each of a series of 12 strips when the electrodes were half an inch broad, showed that about double the action took place at the positive as at the negative end, and that there was a minimum in the middle. The influence of the direction of the strip was also investigated. When it was put directly across the line joining the electrodes, there was no action nor did the transverse strip affect the action of the others.

VII. A longer strip gives increased action.

VIII. The influence of the conductivity of the material of the strip is shown.

IX. Also the influence of the chemical activity of the metal. These numbers were obtained, expressive of the relative activity—

| | |
|---|---|
| Zinc | 19·5 |
| Aluminium | 15·2 |
| Copper | 1·7 |
| Lead | 1·6 |
| Silver | 1·3 |
| Platinum | 1·0 |

X. By the use of strips the electrical condition of the different parts of an electrolyte was demonstrated. The electric influence is shown to spread out in a manner much resembling the magnetic field.

M. W. W.

**The Replacement of Electro-positive by Electro-negative Metals in a Voltaic Cell.** By J. H. GLADSTONE and ALFRED TRIBE (Proc. Roy. Soc., 1875).

THE chemical theory of galvanism supposes that the force originates in the chemical action which takes place between the zinc and acid; the contact theory that it originates in some unexplained manner in the opposite electrical condition of the two metals induced by their contact. If the chemical theory be the true one, it is evident that a zinc-platinum cell can become active only when the binary liquid contains hydrogen or some metal which is less powerful than zinc. If for instance a potassium salt were employed instead of a hydrogen compound, it is inconceivable on the pure chemical theory that there should be any action at all.

The authors found that a zinc-platinum pair immersed in potassium chloride solution, liberated potassium against the platinum plate, as evidenced by the evolution of hydrogen and the presence of free alkali. The experiment also succeeded with the chlorides of sodium, ammonium, barium, strontium, calcium and magnesium.

This action is slow, but upon substituting magnesium for zinc, it becomes very decided. Quantitative experiments are given, in which a magnesium-platinum pair was used with the chlorides of potassium and sodium.

Sulphates and nitrates are also decomposed, and it is found that a metal when joined to another more electro-negative will decompose its own salts. For instance, mercury and gold decompose chloride of mercury, metallic mercury being deposited upon the gold.

M. W. W.

**Action of the Electric Current on Fused Amalgams and Alloys.** By E. OBACH (Chem. Centr., 1875, 497).

THE experiments were made with sodium amalgam and with alloys of potassium with sodium, and of tin with lead. The results, however, were negative, the portions in the neighbourhood of both the poles employed for passing the current being identical in chemical composition, and in physical properties.

C. E. G.

**Researches on the Conduction of Heat in Gases. Part II.** By STEFAN (Chem. Centr., 1875, 529).

THIS paper contains the results of determinations of the relative conductivity of different gases for heat. The method employed was the same as that adopted for the determination of the conducting power of air, which was published in Part I. The experiments were conducted upon the following gases:—Carbonic acid, nitrous oxide, olefiant gas, carbonic oxide, air, oxygen, marsh-gas, and hydrogen. The rapidity with which a hydrogen thermometer or an air thermometer will cool in these different gases is in the following ratios: 0·64, 0·66, 0·75, 0·98, 1,

1·02, 1·37, 6·72, and these numbers show approximately the relation between the conducting power of these gases for heat.

H. H. B. S.

**Remarks on the Conduction of Heat by Gases.** By L. BOLTZMANN (Chem. Centr., 1875, 754, from the Wien. Anz., 1875, 174).

THE author enters into some considerations on the researches of Stefan, Kundt, Warburg, and Winkelmann. Stefan has already remarked that these observations seem to indicate that the intra-molecular movement is not connected with the conduction of heat to so great a degree as Maxwell supposed. It is shown that it closely agrees with practical knowledge to assume that the share which the intra-molecular movement furnishes to the total conduction of heat amounts to only about $\frac{3}{15}$ths of that which it would be according to Maxwell's hypothesis; and it is remarked that this is much less than the intra-molecular movement would contribute to the conduction of heat in consequence of the mere diffusion of the molecules, supposing that in each zone the relation of the working force (*vis viva*) of the progressive and intra-molecular motions is the same as in an uniformly warmed gas of the same temperature.

H. H. B. S.

**On the Equilibrium of Temperature of Gases upon which Exterior Forces act.** By L. BOLTZMANN (Chem. Centr., 1875, 754, from Wien. Anz., 1875, 174).

THIS paper contains the proof that in the case of the action of exterior forces, a function exists the value of which, in consequence of the molecular movement, cannot increase, and which therefore, for the equilibrium of temperature, must have a constant minimum value.

H. H. B. S.

**Application of the Mechanical Theory of Heat to the Study of Volatile Liquids. Simple Relations between Latent Heat, Molecular Weight, and Vapour-tension.** By R. PICTET (Compt. rend., lxxxii, 260).

FROM the considerations explained in the memoir, the following five laws are deduced:—

1. For all liquids, the cohesion is a constant number.
2. The derivative of the Napierian logarithm representing the ratio between vapour-tension and temperature, is constant for all liquids, when they are compared under the same circumstances of pressure and temperature.
3. The latent heat of all liquids referred to one and the same pressure, multiplied by the molecular weight referred to an uniform temperature, gives a constant product.
4. For all liquids, the difference between the internal latent heat at

any two temperatures multiplied by the molecular weight, is a constant number.

5. The latent heat of every liquid is a multiple of its specific heat.

J. W.

**The Dispersion of Heat in Bodies, and its Relation to the Structure of Minerals.** By ED. JANNETTAZ (Jahrb. f. Min., 1876, 199).

THE author comes to the following conclusions:—The plane parallel to the direction of perfect cleavage is also that of easy separation. The direction of separation of stratified bodies does not appear to be influenced by the law of the expansion of heat in natural bodies built according to the same molecular type; such as the amphiboles and pyroxenes. It is highly interesting to notice the coincidence of the thermal properties of the varieties of amphibole and pyroxene whilst they differ so much in chemical composition. Similar forms, cleavage, and position of axes seem to ensure similar thermal properties.

C. A. B.

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**Freezing Mixtures.**

By L. PFAUNDLER (Chem. Centr., 1875, 738).

THE author has already shown (this Journal, 1876, i, 867), that on mixing sulphuric acid of 66 per cent. with snow, a minimum temperature of $-37°$ is reached, the initial temperature of the materials being 0°. From theoretical reasoning he concluded that if the initial temperature of the materials were lowered, the minimum temperature attained on mixing these materials would be likewise lowered. By pouring acid over snow in a high cylinder the upper layers of acid and snow quickly attain a temperature of $-37°$: a series of layers is formed, the temperatures of which increase from the upper downwards: but the excess of acid in contact with the upper layer has now reached a temperature of $-37°$: hence as it percolates downwards and comes into contact with very cold snow, a temperature considerably under this point is attained. A similar result may be attained by causing acid of 66 per cent. to ascend through a tube surrounded with snow, and then to pour on to the upper surface of this snow: temperatures of $-50°$ to $-60°$ may thus be readily reached.

M. M. P. M.

**Temperature of Steam.** By L. PFAUNDLER (Chem. Centr., 1875, 689).

ACCORDING to the author's experiments, the temperature of the steam from a saline solution is probably lower than that of the liquid, even when external cooling influences are removed. He advances an hypothetical explanation of the fact, based upon the dynamical theory of gases.

R. R.

**On the Thermic Effect Produced by Dissolving Nitrate of Ammonium in Water, and on the Value of this Salt for Freezing Mixtures.** By J. TOLLINGER (Chem. Centr., 1875, 753).

THIS is a short abstract of a paper from the *Wien. Anz.* (1875, 172). In the original paper the results of the author's investigation are stated in two tables, the one showing the data in connection with the mixture of nitrate of ammonia and water, and the other those referring to the mixing of nitrate of ammonia with snow.

H. H. B. S.

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**On the Affinities Developed during the Slow Oxidation of Hydrogen and Carbonic Oxide by Platinum.** By ERNST VON MEYER (J. pr. Chem. [2], xiii, 121—158).

VARYING volumes of hydrogen and carbonic oxide were mixed with oxygen in quantities insufficient for complete combustion, and a ball of carbon containing platinum-black was introduced into the mixture. In some cases an indifferent gas (nitrogen) was also added.

It was found that the oxygen first united with the carbonic oxide, and that considerable quantities of hydrogen were oxidised only after the carbonic oxide was reduced to a minimum. In this respect the action of the carbonic oxide may be compared with that of antiseptic bodies, for just as these (acids for instance) are robbed of their power by being brought into some combination (*e.g.*, by neutralisation), so is the carbonic oxide rendered inert by conversion into carbonic acid.

The relative proportion of the two gases which are oxidised does not vary regularly, but goes by bounds, and in such a way that in distinct intervals of time the quantities of carbonic oxide and hydrogen stand to each other in simple molecular proportions. Experiments on the imperfect combustion of the two gases by *explosion* with an insufficient quantity of oxygen showed that the affinity of the hydrogen for oxygen was 3·14 times greater than that of carbonic oxide for the same gas. But when platinum is used to bring about the union of the gases, the affinity of the carbonic oxide was found in some cases to be 7·06 to 7·75 times greater than that of hydrogen: or taking the affinity of hydrogen to oxygen as the unit, the affinity of a molecule of carbonic oxide for oxygen on slow oxidation by platinum was 22·2 to 24·3 times greater than when the union was brought about by explosion.

The affinity of the carbonic oxide for oxygen is diminished when the quantity of oxygen is increased, the proportion of hydrogen to carbonic oxide remaining constant. The quantity of carbonic oxide in proportion to that of hydrogen appears (within certain limits) to exercise less influence on the relative affinity of the two gases for oxygen; but, on the other hand, the presence of nitrogen increases the affinity of carbonic oxide for oxygen, or lessens that of hydrogen, whether the oxidation is brought about instantly by explosion or slowly by platinum. The action in this case is probably mechanical. The oxidation of carbonic oxide is favoured by the continual removal of the carbonic acid formed. The affinity of hydrogen for oxygen in

comparison with that of carbonic oxide, was found to be increased by elevation of temperature, but in this case also by bounds, for the law of oxidation in molecular proportions holds good for higher temperatures. To explain the fact that the carbonic oxide is oxidised before the hydrogen in the mixture of gases, the author supposes that carbonic oxide is much more strongly attracted than hydrogen by the molecules of the platinum, which then becoming surrounded by an atmosphere of carbonic oxide, do not come freely in contact with the hydrogen. When the carbonic oxide has been oxidised, the hydrogen molecules have free access to the exterior surface of the platinum molecules. Elevation of temperature increases the molecular motions of the gases and loosens the (hypothetical) atmosphere of carbonic oxide surrounding the platinum, and thus allows the hydrogen molecules to come within the sphere of activity of the platinum. The addition of an indifferent gas like nitrogen does not essentially lessen the attraction of the platinum molecules for those of carbonic oxide, whilst it does prevent the impact between the platinum and hydrogen molecules.

G. T. A.

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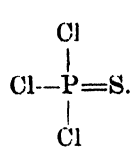
**On the Influence of Pressure and Strain upon the Thermal Coefficient of Expansion of Bodies, and on the Relative Behaviour of Water and Caoutchouc.** By C. PUSCHL (Chem. Centr., 1875, 561).

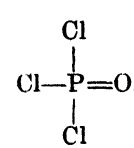
THE coefficient of expansion of a fluid or of a solid is generally diminished by compression, and increased by dilatation. The behaviour of water is, however, peculiar in this respect. Its coefficient of expansion is found to increase with the pressure, and it will therefore follow that the temperature of its maximum density will diminish with the pressure. According to Schmulewitsch the coefficient of expansion of caoutchouc becomes, at a certain tension, zero, and at a greater tension negative.

H. H. B. S.

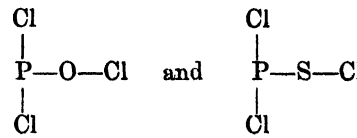
**Researches upon the Specific Volume of Liquids.** By T. E. THORPE (Phil. Mag. [5], i, 554).

1. *The Atomic Value of Phosphorus.*—If the variation in the specific volume of oxygen and sulphur, in combination, be due to the manner in which those elements are held in union (as assumed by the accepted theory), it is possible to decide, in the case of the thio-chloride and oxychloride of phosphorus, the atomicity of the phosphorus therein combined. If the phosphorus be a pentad, the formulæ of those bodies would be written



By the determination of the specific gravity, boiling point, and rate of expansion of $P.Cl_3$, $P.O.Cl_3$, and $P.S.Cl_3$, the author decides that the specific volume of the oxygen and of the sulphur in the two latter bodies, corresponds with the values given by Kopp for those elements when in combination, "without the radicle," from which it would appear that in the compounds mentioned the phosphorus exists as a triad, and that their formulæ should consequently be written



C. H. P.

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**Hygrometric Diffusion.** By L. DUFOUR (Chem. Centr., 1875, 643).

WHEN a porous partition separates two masses of air in different hygrometric conditions, it is traversed by inverse but unequal diffusion currents, the stronger of which goes from the drier into the moister air. The difference between these currents depends chiefly upon the difference of the tensions of the aqueous vapour. This diffusion takes place even through plates of marble 5 mm. thick; and, more slowly, through alabaster. When air in a hygrometric state different from that of the external air, is enclosed in a vessel having part of its walls porous, the diffusion produces a difference of pressure, which is independent of the extent of porous surface, but is longer in attaining its limit as the surface of the porous partition is smaller. In the case of porous earthenware this pressure-difference is inversely proportional to the square root of the thickness of the porous septum. The excess of the current from the drier air is greatest when the pressures on each side of the partition are equal, and it varies with the nature of the partition, and with the hygrometric conditions.

R. R.

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**Determination of the Elasticity of Regular Crystals in Different Directions.** By P. GROTH (Jahrb. f. Min., 1876, 199—200).

THE experiments made by Voigt for this purpose by determining the tenacity of the crystal in different directions, gave for the relation between the minimum and maximum elasticity the ratio 1 : 1·22. The transmission of sound in solid bodies was found by Groth to be dependent upon their elasticity. He determined the relation between the minimum and maximum elasticity of rock-salt by means of "nodal lines," produced upon a rod of the same, 80 mm. long and 2 mm. thick, and found it to be as 1 : 1·19. This determination proves the correctness of Voigt's results, which were obtained in an entirely different way. The difference between the condition of regular crystals and amorphous bodies is therefore apparent.

C. A. B.

**The Unequal Solubility of the Different Surfaces of the same Crystal.** By L. PFAUNDLER (Chem. Centr., 1875, 498).

THE author explains the phenomenon of a crystal changing its shape without alteration of weight in a saturated solution of the same substance at a constant temperature, by supposing that when the molecules in the liquid come in contact with the crystal molecules, they may either be reflected, they may adhere, or they may tear away some of the latter. As the crystal does not alter in weight, it follows that as many molecules adhere as are torn away, and if the average energy of vibration were the same on all the surfaces of the crystal, and in all directions, the crystal would not alter in form. If, however, it is not equal on all the surfaces, some will present less resistance to the molecular action and will decrease, whilst the others, at which it is greater, will increase, and thus the crystalline form will be altered without any change of weight.

C. E. G.

**On the Sudden Cracking of Glass.** By ED. HAGENBACH (Pogg. Ann., clv, 479—480).

THE author having examined, by polarised light, the fragments of two glasses which had suddenly cracked without any apparent cause, noticed in both cases the prismatic colours discovered by Seebeck. On submitting a number of sound glass articles to a similar examination he observed traces of colour in a few cases only. He suggests that glass wares should be examined in this way, those being rejected which distinctly exhibit these colours.

H. H. B. S.

## Inorganic Chemistry.

**Decomposition of Water by Platinum.** By H. ST. CLAIRE DEVILLE and H. DEBRAY (Compt. rend., lxxxii, 241—243).

WHEN potassium cyanide is heated with spongy platinum, in presence of water vapour, to a temperature of 500°—600°, hydrogen is disengaged and a double cyanide of platinum and potassium is formed. The principal reaction may be represented as follows :—

$$4KCN + 2H_2O + Pt = Pt(CN)_2.2KCN + 2KHO + H_2.$$

Since a molecule of potassium cyanide absorbs during decomposition 86·7 kilogram-degrees of heat, and a molecule of water vapour 28·8 kilogram-degrees, the quantity of heat absorbed in the above reaction will be 115·5 kilogram-degrees: and since the quantity of heat evolved by the combination of potassium with one molecule of oxygen and one molecule of water vapour is 75·5 kilogram-degrees, it is necessary, if the heat disengaged during the reaction is to exceed the heat absorbed,

that more than 40 kilogram-degrees should be set at liberty by the combination of the platinum with cyanogen and potassium cyanide.

Berthelot has observed that iron under similar circumstances disengages an amount of heat equivalent to 67 kilogram-degrees; it is probable, therefore, that platinum would disengage at least 67 kilogram-degrees, since it displaces iron from its combinations with cyanogen. If this low number be chosen, the total heat evolved in the reaction would be 142·5 kilogram-degrees, and the difference between the heat evolved and the heat absorbed 27 kilogram-degrees. There can be little doubt, therefore, but that the formation of the caustic potash plays an important part in the decomposition, inasmuch as a large development of heat is thereby produced.

A concentrated solution of potassium cyanide also dissolves platinum with evolution of pure hydrogen, and with formation of the double cyanide as in the previous instance. By calculating the amount of heat which takes part in this latter reaction, from the same data as before, a difference of 25 kilogram-degrees is observed against 27 kilogram-degrees, found by the previous method of operating.

J. W.

## On the Exchanges of Ammonia between Natural Waters and the Atmosphere. By Th. Schlœsing (Compt. rend., lxxxii, 747).

It is found by a series of experiments that when the quantity of ammonia in the air is about equal to that usually found therein, the exchanges of ammonia between the air and the waters are regulated by the law of absorption; the amount of ammonia condensed by each unity by weight of water increases, as the temperature lowers.

C. H. P.

## Amidosulphonic Acid. By Emil Berglund (Deut. Chem. Ges. Ber., ix, 252—256).

By acting on chlorosulphuric acid ($HOSO_2Cl$) with ammonia, a body is obtained which the author considers to be the ammonium salt of an acid of the formula:

$$\begin{matrix} HO.SO_2 \\ HO.SO_2 \end{matrix}\!\!>NH.$$

and which might be called *imidosulphuric acid.*

This salt, the formula of which is $(H_4N)_2O_2(SO_2)_2NH$, is identical with the parasulphatammonium of Rose (*Pogg. Anal.*, xlvii, 471, xlix, 183), Jaquelin's sulphamide (*Ann. Chim. Phys.* [3], viii, 293), and Woronin's acid ammonium sulphamate (*Zeitschr. f. Chem.*, 1861, 54). Imidosulphonic acid is tribasic, for the hydrogen in combination with the nitrogen can, though not with the same facility as the other two atoms, be exchanged for positive radicles. The salts formed have the formula $R_2O_2(SO_2)_2NR$, are characteristic, and at times well crystallised. Besides these another series may be obtained with the formula $R_2O_2(SO_2)_2NH$. The first series is basic, the second neutral, and they are all remarkable for the intimate combination between the sulphur

and nitrogen, as is shown by the difficulty of converting them into sulphate by the action of barium chloride, and by the fact that the nitrogen is expelled only on ignition with soda-lime.

The neutral salts are in general easily soluble: only those of ammonium, potassium, and barium are crystallisable. The potassium salt is distinguished by its difficult solubility, and is interesting as being identical with Claus' potassium disulphammonate (*Lieb. Ann.*, clii, 335, clviii, 53 and 194).

The basic salts are much more stable and more insoluble than the neutral ones. They are mostly crystallisable, and on treatment with even weak acids pass into neutral salts. An interesting series of salts may be obtained with the general formula $K_2O_2(SO_2)_2N.Hg.N(SO_2)_2O_2R_2$ where the mercury is retained with considerable force. These might be called salts of *mercur-imidosulphonic acid*, $H_4O_4(SO_2)_4N_2Hg$, more especially as this body can be obtained in the free state by treating the salt $Ba_2O_4(SO_2)_4N_2Hg$ with an equivalent quantity of sulphuric acid.

G. T. A.

## Some Compounds of Tellurium. By F. Becker (Liebig's Annalen, clxxx, 257—268).

The author prepares pure tellurium by distilling the crude substance in a current of hydrogen. In this process combination of hydrogen with tellurium takes place to a slight extent.

*Telluric acid* is prepared very conveniently and without loss by the following process:—Finely powdered tellurium is dissolved in excess of dilute nitric acid, care being taken to avoid rise of temperature, whereby tellurous anhydride would be precipitated. Lead peroxide is then added in slight excess, and the solution is boiled till a few drops of the filtered liquid gives no brown colour with stannous chloride. The filtrate is freed from lead by sulphuric acid not in excess, and from nitric acid by evaporation over the water-bath; and the residue, after digestion with alcohol and ether to remove the last traces of sulphuric acid, is purified by repeated crystallisation in a partial vacuum.

*Tellurium and Sulphur.*—The precipitates produced by hydrogen sulphide in solutions of tellurous and telluric acids are not tellurium sulphides, as was thought by Berzelius, for when the precipitates are digested with carbon bisulphide, nearly the whole of the sulphur is extracted. They must, therefore, be regarded as mixtures, not compounds, of sulphur and tellurium:

$$TeO_2 + 2H_2S = Te + S_2 + 2H_2O\,;$$
$$TeO_3 + 3H_2S = Te + S_3 + 3H_2O.$$

The author thinks that sulphides are formed at first, but immediately decomposed.

*Tellurium Tartrate.*—Tellurous acid dissolves readily in solution of tartaric acid. The solution, when allowed to evaporate spontaneously, yields long pointed transparent crystals, which effloresce in the air, turning white and opaque. Their composition, after drying at 100°, agrees with the formula, $(C_4H_5O_6)_4Te$.

*Triethyl-tellurium Iodide.*—Tellurium ethyl and ethyl iodide combine together to form this compound, which crystallises in large pale-yellow oblique rhombic tables and prisms. It dissolves easily in cold water and alcohol but not in ether. Melts at 90°—92°, and solidifies again at 86°. Its composition agrees with the formula $Te(C_2H_5)_3I$. It is rapidly decomposed by strong sulphuric acid, a little hydrogen telluride being evolved.

When a solution of triethyl-tellurium iodide is digested with freshly precipitated silver oxide, a strongly alkaline liquid, which refuses to crystallise, is formed. On addition of hydrochloric acid and platinum chloride it gives at once an orange-red crystalline precipitate of *triethyl-tellurium platinochloride.* $Te(C_2H_5)_3Cl.PtCl_4$. This substance is insoluble in alcohol and ether, sparingly soluble in water.

J. R.

## Titanium Compounds. By C. Friedel and J. Guérin (Compt. rend., lxxxii, 509—512).

*Titanium Oxychloride*, $Ti_2O_2Cl_2$.—This compound may be obtained in brownish-red crystals, which are not immediately attacked by water, or even by dilute nitric acid. When, however, they are exposed for some time to the air they become white and are transformed into titanic acid. They are attacked by ammonia, which first blackens them, but afterwards they become white, still retaining their shapes; at the same time there is an evolution of hydrogen. Heated in the air they are decomposed, giving off vapours of tetrachloride of titanium and leaving a residue of titanic acid.

*Titanium Sesquioxide*, $Ti_2O_3$—This, like the former, is a product of the reaction of hydrogen and titanium chloride upon titanic acid. It is obtained in the form of minute red crystals, which the authors find to be isomorphous with those of the oligist of Elba. They conclude that there exist three isomorphous compounds, $Fe_2O_3$, $FeTiO_3$, and $Ti_2O_3$, and that the constitution of titaniferous irons is explicable as a mixture of the first two, but they consider that these facts would not, of themselves, justify the withdrawal of titanium from the companionship of silicon and tin with which it is commonly classed.

R. R.

## A New Property of Aluminium. By E. Ducretet (Chem. Centr., 1875, 738).

If an aluminium plate be made the negative pole of a galvanic circuit while the positive pole consists of a platinum plate, acidulated water is quickly decomposed by the arrangement, but if the position of the plates be reversed by making the aluminium the positive pole, the water is now decomposed very slowly. An iron wire communicating with the two poles in the first arrangement is readily fused, but in the second is scarcely raised in temperature. The author promises further investigation on this subject.

M. M. P. M.

**On the Blue Colour of Retorts employed in the Distillation of Zinc.** By C. DEGENHARDT (Chem. Centr., 1875, 511).

AFTER being used for a short time, these retorts acquire a blue colour, the intensity of which increases with the temperature. An analysis of a blue retort gave $SiO_2$, 41·13; $Al_2O_3$, 33·48; $Fe_2O_3$, 2·84; ZnO, 21·47; MnO, 0·37; CaO, 0·92; MgO, 0·47; whilst a nearly white one gave $SiO_2$, 50·10; $Al_2O_3$ 38·28; $Fe_2O_3$, 3·42; ZnO, 6·10; MnO, 0·41; CaO, 1·13; MgO, 07·3. An analysis of several specimens showed that the darker the colour the higher was the percentage of zinc: this does not combine with the silica, as the latter may be removed by hydrofluoric acid without destroying the colour. The zinc oxide is probably combined with the alumina, as in gahnite.

C. E. G.

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**A New Oxide of Manganese.** By É. FREMY (Compt. rend., lxxxii, 475).

ON pouring a saturated solution of manganous sulphate into excess of an acid solution of manganic sulphate (prepared by treating potassium permanganate with sulphuric acid), a red liquid is formed, from which deliquescent unstable crystals may be obtained. The base of this new salt is considered by the author to be an oxide intermediate between the monoxide and the sesquioxide of manganese [manganoso-manganic oxide]. The same salt appears to be sometimes formed in small proportions, when oxide of manganese is treated with sulphuric acid, as in the preparation of oxygen.

R. R.

**Preparation of Platinum Black by means of Glycerin.** By R. ZDRAWKOWITCH (Bull. Soc. Chim. [2], xxv, 198).

IF a mixture of 15 c.c. of glycerin and 10 c.c. of caustic potash of specific gravity 1·08 be heated to boiling, and then 3 to 5 c.c. of solution of platinic chloride be dropped in, the platinum-black thereby produced is possessed of very great catalytic energy. If an excess of potash be used, a platinum mirror is obtained by careful heating.

C. H. P.

**Silication of Platinum and certain other Metals.** By J. B. BOUSSINGAULT (Compt. rent., lxxxii, 591—596).

A SERIES of experiments undertaken to determine the cause of the increase of weight which platinum undergoes when heated in a silica crucible lined with carbon, show that the increase is due entirely to silicon derived from the crucible,—previous experiments having shown that if silica be heated with carbon to a very high temperature, and then cooled in an atmosphere of hydrogen, no free silicon is found in the mixture.

The conclusions drawn from the whole of the results are as follows:—

1. That under the conditions of the experiments platinum, ruthe-

nium, iridium, or palladium, heated to redness in pure carbon, were not carburised.

2. At a very high temperature silica is reducible by carbon.

3. In a mixture of carbon and silica heated to whiteness, and into which platinum is introduced, the metal does not exercise an action of contact, determining the reduction of the silica; but its operation is limited simply to the removal of the silicon at the same rate as this is produced.

The production of chloride of silicon by passing chlorine through a heated mixture of carbon and silica is due to a precisely similar action.

4. If after heating a mixture of silica and carbon, and cooling it out of contact of air, no free silicon is found, it is because the silicon is carried away by the gases,—among which probably carbon monoxide dominates,—its stability appearing not to be absolute; and the proof of this is that if a sheet of platinum be held at a distance of 1 centimeter above the brasque from which the silicon is proceeding, the platinum becomes silicurised.

C. H. P.

**Removal of Arsenic from Sulphuric Acid.** By R. WAGNER (Chem. Centr., 1875, 722).

THORN's method (this Journal, 1876, i, 518), gives good results; the author, however, gives the preference to the use of sodium sulphide. By using barium thiosulphate the whole of the arsenic is precipitated as sulphide, without the introduction of any foreign substance into the sulphuric acid.

M. M. P. M.

**Occluded Hydrogen in so-called Explosive Antimony.** By R. BÖTTGER (Chem. Centr., 1875, 674).

THE metallic-looking deposit which is obtained at the negative pole on electrolysing a hydrochloric acid solution of antimony chloride, and was formerly supposed to consist of antimony in a peculiar allotropic condition, was some time ago shown by the author to contain chloride of antimony, and he has now discovered that this curious product also contains occluded hydrogen.

R. R.

**Crystals in Glass.** By O. SCHOTT (Pogg. Ann., clv, 422).

THE author has had an opportunity afforded him of studying the phenomenon of the "devitrification of glass" in its different stages of development. He believes that the tendency to devitrify depends upon the proportion of amorphous and crystalline substances, and therefore generally upon the amount of lime present. Since silicate of lead becomes amorphous on cooling, lead glass cannot devitrify. Diagrams are given of the different crystalline forms met with in devitrified glass.

H. H. B. S.

# Mineralogical Chemistry.

## On a Newly-discovered Deposit of Silver-ores in the Troitzker District of the Government of Orenburg. By W. von Beck (Jahrb. f. Min., 1876, 162—170).

The silver-ores occur in a quartz vein which has an almost vertical position, with a strike towards the north-west, and an inclination of 70°. This vein penetrates a white crystalline schist which is decomposed for a distance of 8·5 meters from the point of penetration, the result being the formation of a white talc and mica-clay. At a farther distance the rock has a decided slaty texture and is a mixture of talc, mica, quartz, and some felspar. The vein-quartz is very hard, partially vitreous, and coloured by ferric oxide and arsenical compounds; the silver-ore has not yet been found in the quartz itself, but occurs in ochreous bands enclosing the vein. The silver is combined with chlorine, bromine, and iodine, and these combinations are sometimes observed occurring in almost microscopical crystals, which (according to Professor Jeremejew) are rhombic octahedrons. Besides the crystals, extremely thin deposits and crust-like plates of these silver compounds are found; also native silver in scales, and sometimes accompanying them are deposits of earthy malachite. The thickness of the bands (which do not occur equally on both sides of the vein) is very variable, ranging from a mere film to 17 centimeters, and is generally inversely proportionate to the thickness of the quartz-vein. The ore occurs in nests or pockets, both in the "dip" and "strike" of the vein, but has only been worked to a depth of 19·2 meters and for 53 meters in the direction of the "strike;" nevertheless 81 kilos. of silver of excellent quality have been obtained. The silver was obtained from the ore by the "amalgamation process;" it was also observed that the temperature of the air, and the water used in washing the ore, had a great influence on the results of the process; as in summer, the duration of the process was 8 hours and in winter 16. The amount of silver present was 25·6 grains in 16·38 kilos. of ore.

Similar silver-ores occur in Chili, Mexico, and Spain, where they are famous for their richness, which increases with the depth. This may prove to be the case with the Russian mines, as at present the greatest depth attained is only 230 feet. Some difficulty was experienced in obtaining pure specimens of the ore, as the microscopical crystals and crust-like plates were found to have a grey tarnish on their surface, whilst their interior exhibited a dark yellowish-green colour. The mineral is malleable, soft enough to receive impressions of a finger-nail, and has a resinous lustre; fuses easily before the blowpipe to a yellowish-green globule, the flame being tinged blue at the first impact with the assay. Strong ammonia dissolves it partially, but on the addition of nitric acid in excess gives rise to a yellow precipitate consisting of silver chloride and bromide. Silver iodide was obtained only once. An analysis gave the mineral the following percentage composition:—Ag = 63·35, Br = 28·44, Cl = 8·21

= 100·00. It will be seen that the ratios of Cl : Br : Ag are as 2 : 3·06 : 5·30, so that it may be assumed to be a combination of 3 atoms of AgBr with 2 atoms of AgCl. A second variety of this mineral occurs in the bands along with the other variety already described. It is an amorphous mass, of a dark liver-brown colour passing into deep indigo-blue, occurring sometimes in large impure masses mixed with much ochre and quartz, or in the form of spherical enclosures having a foliated texture mostly of a deep indigo-blue colour, and often attaining the size of a pea. Sp. gr. = 3·064. A qualitative analysis showed that it contained silver, ferric oxide, calcium, bromine, arsenic acid, water, and traces of silica. On heating the mineral in a tube closed at one end water is first evolved and then a sublimate of arsenious acid is formed. Three methods of quantitative analysis were employed.

1st. The mineral was treated with caustic soda and chlorine gas, and the arsenic acid thus formed estimated as ammonium-magnesium arsenate. The amounts of the other constituents were determined in the usual way.

2nd. The mineral was decomposed by means of hydrochloric acid and potassium chlorate, and the arsenic precipitated as sulphide and determined.

3rd. The mineral was placed in a small porcelain boat enclosed in a glass tube and heated in a stream of sulphuretted hydrogen. The sublimed arsenic sulphide was collected in ammonia, but no good results were obtained, as the amount of arsenic acid was eventually obtained by difference. Subjoined are the author's results :—

| | (AgCl and AgBr + $SiO_2$) | CaO. | $Fe_2O_3$. | $AsO_4$. | $H_2O$. |
|---|---|---|---|---|---|
| No. 1. | 5·78 | 2·18 | 36·80 | 42·37 | 13·43 = 100·56 |

| | (AgCl. AgBr and $SiO_2$, &c.) | CaO. | $Fe_2O_3$. | $AsO_4$. | $H_2O$. |
|---|---|---|---|---|---|
| No. 2. | 6·41 | 2·07 | 36·73 | 41·44 | 13·43 = 100·48 |
| No. 3. | 9·25 | 1·48 | 35·40 | 40·44 | 13·43 = 100·00 |

If the calcium oxide and the silver salts be considered as impurities, and deducted from the other constituents, the following percentages are obtained: —

| | Ferric Oxide. | Arsenic Acid. | Water. |
|---|---|---|---|
| No. 1..... | 39·74 | 45·75 | 14·50 |
| 2..... | 40·09 | 45·24 | 14·66 |
| 3..... | 39·65 | 45·30 | 15·04 |

On comparing these amounts with the known percentage composition of scorodite, it seems probable (according to the author) that the new mineral is scorodite, mixed with hydrated ferric oxide and silver compounds.

C. A. B.

**The Crystallographic System of Muscovite.** By G. TSCHERMAK (Jahrb. f. Min., 1876, 196).

ON examining crystals of this mineral from the lower Sulzbachthal, in the Pinzgau, it was found that the plane of the optical axes, which, as is well known, runs parallel with the longer diagonal of the basal terminal plane, is not exactly perpendicular to the latter plane; but has an upward anterior inclination, when the crystal is placed in the usual position. The apparent angle which is formed by the plane of the axes with the most complete cleavage-face (0P) was found to be 88° 15′ for yellow light. A measurement of a cleavage plate of Bengalese muscovite gave the angle 88° 20′ for yellow light. The author contends, therefore, that muscovite crystallises in the monoclinic system.

C. A. B.

**Microscopical Examinations of thin Sections of compact Garnet.** By A. WICHMANN (Jahrb. f. Min., 1876, 198—199).

ON examining specimens of compact garnet from Berggiesshübel and the Teufelstein, near Schwarzenberg, in Saxony, they were found to consist of irregularly formed granules, and also of distinct crystals, sometimes imbedded in calcite or quartz. The granules do not exhibit any peculiarity, but the crystals appear mostly as hexagonal sections, with a very distinct characteristic shell-like formation. Examined in polarised light, the innermost crystal kernel appears quite dark, whilst the surrounding crystal shells exhibit the most beautiful colours in the alternate zones. Each of the shells exhibit independently the same colour as the others, and two opposite systems always show the same phenomena. Similar colours were observed on examining the irregular granules, the innermost garnet kernel appearing dark. In the variety called allochroite found at Berggiesshübel it was observed that the garnet individuals were doubly refracting, and the shell-like structure was only slightly developed; under polarised light the hexagonal sections appeared divided into six equal, sharply defined fields, of which the parallel and opposite ones exhibited the same colours. The author could not account for the double refraction observed by him, and states that the greatest part of the variety called colophonite (particularly that from Arendal) is a species of vesuvianite.

C. A. B.

**Occurrence of Apatite in Norway.** By W. C. BRÖGGER and H. H. REUSCH (Jahrb. f. Min., 1876, 196—198).

APATITE is found on the south coast, between Langesundfjord and the town of Arendal, in veins, the most important of which occur at Oedegarden, in the parish of Bamle, in gabbro rock. This rock has a spotted appearance, and consists of hornblende and labradorite, intersected by veins of a magnesia-mica containing apatite. At Persdal the vein mass in the gabbro is magnetic iron-pyrites, and in it lie many crystals of apatite, exhibiting the characteristic rounding off of the

angles and edges. At Kragerö apatite does not occur in gabbro, but in vein-stocks of hornblende; the centre of the vein consisting principally of coarse radiating hornblende, which often encloses masses of apatite two feet long. These Kragerö veins have a most peculiar and beautiful appearance, being composed of intensely black hornblende, red apatite, light green and grey radiating masses of asbestos-steatite, and rutile. The other veins are either hornblende or granite. It appears that apatite crystals are generally found only in the "magnetic iron-pyrites-hornblende veins." It has, however, been found crystallised in quartz-masses which intersect the layers of hornblendic and micaceous schist of Oestre Kjörrestad, in the parish of Bamle; sometimes in crystals two inches long, exhibiting the combination $\infty$P. 0P. P. Apatite crystals from Oexöiekollen (Snarum) exhibit the combination $\infty$P. $\infty$P2 . 0P . P . 2P2; the variety called moroxite found at Aestesvag, is found in beautiful large crystals, on which the basal terminal plane does not occur; the colours are white, grey, yellow, green, violet, brick-red. The apatite from Oedegarden is penetrated and coloured by a peculiar carbonaceous substance.

*Kjerulfin.*—This mineral occurs at both the localities named above near Havredal, the colours being light flesh-red to brown and whitish-yellow. From crystals found by the author, the crystal system of this mineral was ascertained to be rhombic.

*Esmarkite.*—Occurs at Vestre Kjörrestad, in Bamle, in polysynthetic twins, but as one individual predominates, and innumerable twin laminæ are interposed, the crystals appear to be simple ones. They have a peculiar rounded surface resembling that obtained by fusion, and are often covered with a fine greenish-black crust, which gives them a very peculiar appearance, differing completely from that of felspathic minerals, but approaching that observed on the plagioclases of Bodenmais, Orijärfvi and Lojo. The crystals exhibited the following forms: $\infty$'P'. $\infty$'P'$\bar{3}$. $\infty$P$\breve{\infty}$. 0P . $_{,}$P$_{,}\bar{\infty}$ . 2$_{,}$P$_{,}\bar{\infty}$ . 2'P$_{,}\breve{\infty}$ . $_{,}$P$_{,}$, the types being either tabular through the basal terminal plane, or prismatic. They are twinned according to two laws, viz.; (1st) twin-plane the brachypinacoïd; (2nd) twin axis, the macrodiagonal. Complete basal cleavage, less complete, parallel with the brachypinacoïd. H = 6. Spec. gr. = 2·66. Colour bluish-grey. Pearly lustre on the cleavage planes, resinous lustre on fractures. This mineral is accompanied by hornblende, apatite, and magnetic iron pyrites.

*Hornblende* seems to occur more frequently than other minerals in the veins containing apatite, exhibiting the forms $\infty$P, $\infty\breve{P}$, 2$\breve{P}\infty$, +$\breve{P}\infty$, 0P, P, + 3$\breve{P}$3. Some of them are intergrown with apatite, others covered with small albite crystals.

*Rutile.*—Nearly always accompanies apatite, sometimes occurring in large quantity. One crystal, weighing 1140 grams, exhibited the following combination, $\infty$P$\infty$. $\infty$P. P$\infty$. P3. P; on another, the pyramid P3 was the predominating form.

*Decomposed Enstatite.*—Also generally accompanies apatite, colour leek-green. Resinous lustre. Hardness 2—3. Chemical composition, according to C. Krafft:—

| | $SiO_2$. | $Al_2O_3$. | MgO. | FeO. | CaO. | $H_2O$. |
|---|---|---|---|---|---|---|
| From Oedegarden.... | 37·63 | 1·02 | 30·37 | 4·99 | — | 7·21=101·22 |
| „ Enden ..... | 59·51 | 0·97 | 30·89 | 2·95 | 0·37 | 6·01=100·70 |

Usual combination $\infty$ P. $\infty$ P $\bar{\infty}$. $\infty$ P$\breve{\infty}$. P$\breve{\infty}$. The crystals of enstatite occur often with undecomposed minerals, sometimes enclosing them, and at other times being enclosed by them.

C. A. B.

## Apatite from Untersulzbach. By G. Tschermak (Jahrb. f. Min., 1876, 200—201).

Some magnificent crystals of this mineral have been lately found at this locality of unusual size. They often enclose fine needles of hornblende, but are sometimes perfectly colourless and transparent. They are tabular through 0P. One of them had a breadth of 5 cm., another of 8 cm., caused by the parallel growth of two individuals.

C. A. B.

## Crystallographic Remarks on Gypsum. By H. Laspeyres (Jahrb. f. Min., 1876, 200).

*Twins from Eichstädt, near Merseburg.*—These twins are found in clay; they are sometimes 4 cm. in size, exhibiting the combination, $\infty$P. $\infty\breve{P}\infty$. $-$P; and considerably elongated parallel to the edge of $-$P. There were "juxtaposition" and "penetration" twins observed in every possible variety, according to the usual law. Five figures of these crystals are given by the author.

*Gypsum Crystals from the Papelsberg, in the Siebengebirge.*—Beautiful, large, completely developed crystals occur at this locality in tertiary clay. They are prismatic, parallel to the vertical axis, and broadly prismatic through the clinopinacoid, exhibiting the combination $\infty$P. $\infty\breve{P}\infty$. $-$P, sometimes also P, $\breve{P}\infty$, and $\frac{1}{3}\breve{P}\infty$.

*Gypsum Twins from Eisleben.*—These twins are double cones, formed by juxtaposition, according to the usual law. They closely resemble those from Girgenti; their combination is $\infty$P. $\infty\breve{P}\infty$. $-$P. $+\frac{5}{6}\breve{P}2$. $\frac{5}{9}\breve{P}\infty$. $-\frac{6}{7}\breve{P}\frac{2}{3}$. $-\frac{3}{2}\breve{P}\infty$. The last two are new.

C. A. B.

## Mineralogical Notices. By G. vom Rath (Jahrb. f. Min., 201—202).

1. *The Chemical Composition of the Yellow Augite of Vesuvius.*—The author obtained a splendid bomb, 5 centimeters in diameter, from this locality. The outer crust consisted of sanidine, black augite, a little hornblende, and melanite. Below this crust, which was thin, there was a second zone, composed chiefly of green diopside and biotite; the interior of the bomb, however, was an aggregate of reddish augite, mica, and humite. The augite exhibited the following combination:—

$\infty P . OP . 2\breve{P}\infty . 2P.\breve{P}\infty . \infty\breve{P}\infty . \infty\breve{P}3$. Sp. gr. = 3·233. Its chemical composition was:—

| $SiO_2$. | $Al_2O_3$. | FeO. | CaO. | MgO. | Loss on ignition. |
|---|---|---|---|---|---|
| 53·2 | 1·5 | 2·3 | 23·4 | 19·3 | 0·2 = 99·9 |

which agrees closely with the white or colourless varieties found at Achmatowsk, Orrijärfvi, Gulsjö, &c. A remarkable fact connected with this augite from the Vesuvian bomb, is that the outer crust contains only black augite; the druses of the second zone contain green augite, and those of the interior yellow augite.

2. *A Brookite Crystal from the Gold-washings of Atliansk, near Miask, in the Urals.*—This crystal was the largest and finest ever seen by the author, its length being 11 mm., and its thickness 4 mm. It was particularly rich in the number of faces observed, and afforded ample proof of their rhombic character, which was lately disputed by A. Schrauf. The crystal closely resembled rutile in colour and transparency, the combination being $\infty P . P\breve{\infty} . P . 2P . \frac{1}{2}P . 2P\breve{2} . 5P\breve{\frac{5}{3}} . 2P\breve{4} . \frac{3}{2}P\breve{3} . \frac{1}{2}P\bar{\infty} . \frac{1}{4}P\bar{\infty} . 2P\breve{\infty} . \infty P\bar{\infty} . \infty P\breve{\infty} . 0P$. The pyramids, $2P\breve{4}$ and $\frac{3}{2}P\breve{3}$. are new. From measurements made of this specimen, vom Rath feels confident that brookite crystallises in the rhombic system.

3. *Remarkable Sanidine Crystals found in Drusy Spaces in the Doloritic Lava of Bellingen, Westerwald.*—Small prisms of this mineral were discovered in a druse, together with specular iron and hornblende. These prisms rested on a vertical edge, on the rock, and from their occurrence in this way they must all have been simultaneously formed by sublimation. The following faces were observed:—$\infty P . \infty\breve{P}2 . \infty\breve{P}3 . \infty\breve{P}\infty . \infty\breve{P}\infty . 0P . \breve{P}\infty . 2P\infty . \frac{2}{3}\breve{P}\infty$. The clinoprism, $\infty\breve{P}2$, has never been observed before. It is also unusual to find sanidine in doleritic lava. The chief constituent of this dolerite was labradorite. Sanidine is extremely rare as a sublimation-product in lava, but the author observed a few small crystals (Baveno twins) of this mineral in the matter ejected from Vesuvius, in the eruption of 1872.

C. A. B.

**Some Peculiarities in the Microscopical Structure of Felspars.** By FRANK RUILEY (Jahrb. f. Min, 1876, 202—203).

THE author draws the following conclusions from his investigations:—1st. The reticulated striation observed on compact orthoclase does not penetrate through the cleavable mass. 2nd. There is not sufficient proof that this structure is due to twin formation, as colours are sometimes observed on examining specimens by polarized light; whilst at other times only lines are observed without the colours, which would not be the case if the striation were due to twin-formation only. 3rd. A similar structure is sometimes observed on felspar laminæ, which apparently exhibit parallel striation alone. 4th. The reticulated structure is often observed on felspar laminæ and well developed crystals, only, however, on a very restricted space, whilst the other part of the laminæ or crystals exhibits the usual twin-striation, or else none at

all. In cases of this kind it is scarcely possible to say definitely to which crystal system the felspar under examination belongs. 5th. A peculiar structure is observable in the sanidine crystals of certain trachytes, similar to that observed in sanidine crystals from the Mexican obsidian, and probably identical with the crystalloïds of the "blast furnace slags." As the sanidine twins are really crystals, there cannot be much difference between crystals and crystalloïds, under certain conditions. Although the crystals or crystalloïds of the Mexican obsidian exhibit considerable differences in their internal structure, there can be no doubt about their belonging to the same mineral species. 6th. The present method of distinguishing monoclinic and triclinic crystals cannot be applied with certainty to difficult cases.

C. A. B.

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## Contributions to the Mineralogy of Nova Scotia.

By H. How (Phil. Mag. [5], i, 128—136).

*Centrallassite.*—This mineral, together with two others, cyanolite and cerinite, which were first described by the author in 1859 (*Edinburgh New. Phil. J.*, x, 84), having been placed in a list of "doubtful minerals by a recent writer, the circumstance led the author to a further elucidation of the composition of the first mentioned, and it is shown that it is really a mineral distinct from gyrolite and okenite, with which it was stated to be identical by other writers. The difference is shown by their formulæ:—

| | |
|---|---|
| Okanite..... | $CaO.2SiO_2.2HO$ |
| Centrallassite ..... | $2CaO.3SiO_2.2H_2O$. |
| Gyrolite ..... | $2CaO.3SiO_2.3H_2O$. |

*Stilbite.*—The results of the analysis of a Nova Scotian specimen are placed on record; the percentages agree with the established formula.

*Sphærostilbite.*—Several specimens were collected with perfectly rounded and smooth exterior surfaces, which may properly be placed in this subdivision.

*Cylindroïd of various minerals filling a Vapour-tube.*—A curious specimen, of an external green colour, consisting of a mixture of dissimilar minerals, one of which had the appearance and general characters of stilbite. The green colour was probably due to Poona earth.

*Magnetite.*—Occurs in various veins and pockets in the trap between Blorindon and Brier Island. Frequently massive, sometimes crystallised, generally associated with amethystine quartz crystals.

*Magnetic Hematite.*—Crystallised hematite, showing apparently its derivation from the magnetite. It has the red streak of hematite, and is more or less magnetic.

*Antimony.*—In the course of the analysis of a trap-rock from Margaretville, traces of antimony were found; the form in which it exists is not made out. The metal has not been found in that province (save to a very small extent with galena), but it exists in New Brunswick.

The specific gravities of several specimens of the trap-rock are then

given; one, a columnar trap, sp. gr. 2·994; three crystalline traps from above the amygdaloïd, from 2·962 to 2·915; three amygdaloïd, from 2·747 to 2·659.

C. H. P.

## Rock Interstratified in the Gneiss of Mantiqueire (Brazil). By H. Gorceix (Compt. rend., lxxxii, 688).

A ROCK approaching to epidote, found in the midst of the gneiss which constitutes the major part of the Serre de la Mantiqueire, in the province of Minas Geraes. Its density was 3·4. It melts before the blowpipe to a black slag. Hardness, 6 to 7. Its crystalline form is referred to the oblique prismatic with rhombic base. Its composition was—

| $SiO_2$. | $Al_2O_3$. | CaO. | FeO. | MgO. | Loss on ignition. | Total. |
|---|---|---|---|---|---|---|
| 38·5 | 25·1 | 23·2 | 10·4 | traces | 2·6 | 99·8 |

It is considered to be an epidote in which some portion of the iron exists as protoxide.

C. H. P.

## Analysis of an Edible Earth from the Neograd District in Hungary. By J. Brix (Chem. Centr., 1875, 542).

EARTH eating is known to be practised by various races of people in different countries. In Spain, there is the *bucaro;* in Thuringia, the *beurre de roche;* in Russia, the *farine de roche*, or *farine céleste;* in Hindostan, the so-called *patna-earth;* on the island of Java, a species of earth called *teneampa*, and others, all of which are made use of by the inhabitants as food. At the general meeting of the Hungarian Pharmaceutical Society, in 1875, a note was read by J. Molvar, on a species of earth used as food by the poorer classes of the Neograd district in Hungary in times of famine. The following results show the analysis of this earth:—Carbonic acid, 40·357; lime, 51·488; magnesia, 0·11; volatile matter, 5·545; ferrous oxide, 0·158; alumina, 2·272. As the volatile matter seemed to be the probable means of nourishment, it was subjected to a special examination, and was found to contain, besides empyreumatic substances, 0·067 water, and 0·010 nitrogen.

H. H. B. S.

## Analyses of a Coal from the Island of Suderoë. By Beghin and C. Mene (Compt. rend., lxxx, 1404—1405).

THERE are important beds of coal in this island, one of the Faroe group. By distillation and incineration it gives 46·52 of volatile matters, 51·98 of coke, and 1·50 of ash. Its specific gravity is 1·3531. It occurs in the dolerite rocks, and belongs to the carbons of the tertiary epoch. Its elementary analyses gave—1·052 water; 1·500 ash; 70·672 carbon; 5·148 hydrogen; and 21·628 nitrogen and oxygen.

C. E. G.

**Analysis of the Moritzquelle in Sauerbrunn, near Rohitsch, in South Styria.** By M. BUCHNER (Chem. Centr., 1875, 743).

THE water is very clear, exceedingly sparkling, and has an unpleasant odour. 10,000 parts contained—

| | |
|---|---|
| Potassium sulphate | 0·4068 |
| „ nitrate | 0·0404 |
| Sodium sulphate | 5·2125 |
| „ chloride | 0·4623 |
| „ carbonate | 2·2385 |
| Calcium „ | 9·0230 |
| Magnesium „ | 5·5660 |
| Strontium „ | 0·0044 |
| Iron „ | 0·0505 |
| Aluminium phosphate | 0·0274 |
| Calcium „ | 0·0054 |
| Silicic acid | 0·2270 |
| | 23·2642 |
| Partly combined carbonic acid | 7·5813 |
| Free „ | 23·2387 |
| | 54·0842 |

| | | |
|---|---|---|
| Temperature of water | 11°·3 | 12°·25 |
| „ air | 14°·1 | 21°·2. |
| | | M. M. P. M. |

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**Gases in the Soil.** By J. VON FODOR (Chem. Centr., 1875, 693).

THE author examined the gases drawn from the soil at various depths below the surface by means of iron tubes. The amount of carbonic acid had no relation to the quantity of organic matter, or of moisture, in the soil from which the gases were drawn; but depended upon the permeability of the soil for air, and increased as greater depths were traversed. Important diurnal variations were observable at the depth of 4 meters, and the atmospheric pressure exercised an unmistakable influence, a fall in the barometer coinciding with a rise in the amount of carbonic acid, and *vice versâ*. The permeability of the soil for gases was examined by injecting carbonic oxide gas, and then testing the atmosphere at various points by means of palladium chloride. Changes of atmospheric pressure, the direction and force of the winds, and rain were found to have a perceptible influence on the movements of gases within the soil. The quantity of carbonic acid in the stratum of air next the ground was found to be greater at night than in the day. Augmentations of the amount of moisture at the depth of 4 metres, were noticed about 30 days after the rainfall which caused them.

R. R.

**Carbonic Acid in the Atmosphere.** By FITTBOGEN and HASSELBARTH (Chem. Centr., 1875, 694).

THE average of 347 different determinations made by the authors at Duhme, during a year, gives 3·34 volumes of carbonic acid in 10,000 volumes of air. They cite Schulze's results (2·92, mean of 1600 determinations), and Henneberg's (3·2), as supporting the conclusion that the generally received number (4 to 4·15) founded on Saussure and Boussingault's observations, is probably too high.

R. R.

## Organic Chemistry.

**Source of Carbon Monoxide, characteristic of the Formins and of Polyatomic Alcohols.** By LORIN (Compt. rend., lxxxii, 629—631).

REFERENCE is made to a former paper in which was indicated the analogy between the etherification of ordinary oxalic acid, and a polyatomic alcohol on the one part, and a monatomic alcohol and sulphuric acid on the other.

In the reaction between dehydrated oxalic acid and a polyatomic alcohol, a secondary reaction occurs after some time, whereby carbon monoxide is produced, the yield of formic acid being greater so long as the amount of carbon monoxide remains small, and diminishing as that increases. With erythrite, this does not occur, and it is possible to produce a stronger formic acid than with the other alcohols, and finally, with ordinary oxalic acid no carbon monoxide is evolved at all below 140°.

Characters of the formins—

Case of dehydrated oxalic acid. The abnormal evolution of carbon monoxide which occurs below 100° is due to the decomposition of the formins, serves to characterise this class of ethers.

This is illustrated by treating glycerin, which has served for the production of a large quantity of formic acid, with a final addition of oxalic acid. The quantity of carbonic acid contained in the evolved gases gradually diminishes. As the carbon monoxide increases, the strength of the formic acid diminishes, falling to 54 per cent. when the effect of moderate heat is exhausted.

The residue yields carbon monoxide only with difficulty; but with sulphuric acid that gas is yielded, and its richness in acid, or latent acid, again rises to 25 per cent.

The formic acid obtained gave no traces of allylic products.

Second case, of ordinary oxalic acid.

The distillation was performed on a product resulting from the saturation of glycerin by formic acid from oxalic acid. The distillation, maintained at 130°—135° for three days, yielded much carbon monoxide free from carbonic anhydride, with simultaneous production of 50 per cent. formic acid and water. A residue similar to the former was obtained, containing latent carbon monoxide, and formic acid.

The other polyatomic ethers are no exception to the rule.

*New Method of obtaining Carbon Monoxide.*—When a polyatomic alcohol is saturated with formic acid by means of ordinary oxalic acid, and maintained at 135°, a regular liberation of carbon monoxide takes place. The formic ethers of monatomic alcohols are not decomposed with evolution of carbon monoxide—the decomposition of crude formines becomes characteristic of the polyatomic alcohol.

C. H. P.

**Sources of Carbon Monoxide; New Method of Preparing very Concentrated Formic Acid.** By M. LORIN (Compt. rend., lxxxii, 750—752).

*Action of Heat on Dehydrated Oxalic Acid.*—By heating oxalic acid in an oil-bath for several days, it is completely decomposed, yielding exactly equal volumes of carbonic anhydride and carbon monoxide: the water set at liberty contained but mere traces of formic acid.

*Action of Dehydrated Oxalic Acid on Concentrated Formic Acid.*—At about 105° these two bodies react, yielding carbonic anhydride and carbon monoxide, the latter being always in excess, in the ratio of about two or three to one of carbonic anhydride, from which it is evident that the formic acid is dehydrated by the oxalic acid.

*Action of Formates of Potassium and Sodium on Concentrated Formic Acid.*—If concentrated formic acid be added in equivalent proportions to formate of potassium, dried at 150°, and the biformate heated (after previous cooling), it melts at about 120°, and decomposes, yielding water and carbon monoxide. At 150°—155°, the action is regular, the liberation of the carbon monoxide being simultaneous with the production of aqueous formic acid. The phenomenon repeats itself with each new addition of formic acid to the same formate. Similar results occur with the sodium formate. Formate of barium, and other formates evolve less heat, on admixture, and subsequently the formic acid separates and can be obtained by distillation without production of carbon monoxide. The reaction with formate of ammonium is reserved for future publication.

*Acetates of Potassium or Sodium and Concentrated Formic Acid.*—The admixture with potassium acetate evolved so much heat as to raise the thermometer from 10° to 55°; the resulting salt decomposes regularly at 153°, yielding carbon monoxide, and free formic and acetic acids.

*New Mode of Preparing very Concentrated Formic Acid*—A mixture of sodium formate and oxalic acid, dry, and in powder, yielded nearly the theoretical quantity of formic acid of 99 per cent. Mere traces of carbon monoxide appeared at the commencement of the operation.

C. H. P.

**Action of Monohydrated Sulphuric Acid on Alcohols.** By M. BERTHELOT (Compt. rend., lxxxii, 243—249).

THE heat evolved in the decomposition of various ethereal salts of sulphuric acid by water, has been carefully measured. Two methods

were employed:—1. The alcohol and acid were separately dissolved, without being previously combined. The heat Q disengaged by the union of the acid with the water was first measured; then the heat $Q_1$ produced by the solution of the alcohol in the very dilute acid. 2. The alcohol and acid were weighed into small bulbs, placed in a thin test-tube and the whole immersed in the water of the calorimeter. The bulbs having been broken, the alcohol and acid were allowed to combine, and the ethereal salt was afterwards decomposed by mixing it with the water of the calorimeter.

Let Q′ represent the heat of combination of the alcohol with the acid, and $Q_1'$ the heat produced by decomposition with water, then—

$$Q + Q_1 = (Q' + Q'_1) + x,$$

where $x$ = the heat which would be disengaged if the proportion of ethereal salt remaining in dilute solution were to resolve itself entirely into acid and alcohol. The undecomposed portion can be readily determined by acidimetry.

By the first method the following numbers were obtained:—

$$Q + Q_1 = 219{\cdot}5 + 1455{\cdot}3 = 1669{\cdot}8.$$

By the second method—

$$Q' + Q'_1 = 662{\cdot}15 + 786{\cdot}63 = 1448{\cdot}8.$$

The difference between these two final states corresponds to 1669·8 —1448·8 = 221 kilogram-degrees; which represents the undecomposed ethylsulphuric acid as before mentioned. By titration with baryta-water, 2·211 grams of sulphuric acid were found to remain combined; the initial proportions having been respectively. 3·98 grams of absolute alcohol, and 8·7075 grams of 98 per cent acid.

The accompanying table shows the heat disengaged at 13° by the following transformations:—

I. $C_nH_{2n+1}O$ (dil.) + $H_2SO_4$ (dil.) = $C_nH_{2n+1}HSO_4$ (dil.) + $H_2O$.
II. Dissolution of $C_nH_{2n+1}$ in 100 vols. of water.
III. $C_nH_{2n+1}O$ (pure) + $H_2SO_4$ (liquid) = $C_nH_{2n+1}HSO_4$ (dil.) + $H_2O$.

| | I. | II. | III |
|---|---|---|---|
| Methyl alcohol ..... | − 5·1 | + 2·0 | + 13·8 |
| Ethyl „ ..... | − 4·7 | + 2·54 | + 14·7 |
| Propyl „ ..... | − 4·05 | + 3·05 | + 15·9 |
| Isopropyl „ ..... | − 3·3 | + 3·45 | + 17·1 |
| Isobutyl „ ..... | − 2·2 | + 2·88 | + 17·6 |
| Isoamyl „ ..... | − 0·2 | + 2·8 | + 19·5 |
| Glycerine „ ..... | − 3·2 | + 1·51 | + 15·2 |

Fuming sulphuric acid was also made to act on absolute alcohol, and the heat was measured as in the previous instances. The total acid neutralised, which represents the two isomerides ethyl-sulphuric acid and isethionic acid, having been estimated, the former was destroyed by heating with a volume of standard solution of baryta, and the percentage calculated. 18 per cent. was present as ethyl-

sulphuric acid, and 82 per cent. as isethionic acid. From these data the following equations are deduced :—

$C_2H_6O$ (dil.) + $H_2SO_4$ (dil.) = $C_2H_6O.SO_3$ (dil.) absorbs − 3·4
$C_2H_6O$ (abs.) + $H_2SO_4$ (dil.) = $C_2H_6O.SO_3$ (dil.) „ − 0·9
$C_2H_6O$ (abs.) + $H_2SO_4$ (liquid) = $C_2H_6O.SO_3$ (dil.) + $H_2O$ +16·0

The heat of formation of isethionic acid is therefore almost identical with that of ethyl-sulphuric acid, notwithstanding that the chemical relations of these two isomerides are so essentially distinct.

J. W.

## Sulphuric Ethers.

By M. Mazurowska (J. pr. Chem. [2], xiii, 158—175).

*Diethyl Sulphate.*—When an equivalent of sulphuryl oxychloride is added to two equivalents of ethyl alcohol a brisk reaction takes place; water and hydrochloric acid escape, and a yellowish, inodorous, perfectly neutral liquid is left. This body is miscible in all proportions with water, but at the same time undergoes decomposition and becomes acid. It can be mixed in every proportion with alcohol without decomposition: in ether, benzene, and chloroform a small quantity dissolves, but is reprecipitated by excess of the solvent. Its specific gravity is 1·24. It can be heated on the water-bath without decomposition; at temperatures above 100° carbon separates. Analysis shows that this body consists of diethyl sulphate.

$$SO_2\begin{cases}OC_2H_5\\OC_2H_5\end{cases}.$$

When it is mixed with water, and the solution is neutralised with barium carbonate, transparent, brilliant tabular crystals may be obtained, which consist of barium ethyl sulphate, $(SO_4C_2H_5)_2Ba$. The potassium salt has the formula, $(SO_4C_2H_5)K$.

*Dimethyl Sulphate.*—Prepared in the same way, is a syrupy liquid, which is decomposed by water, dissolves without decomposition in alcohol, is soluble also in ether and chloroform. The barium salt obtained by neutralising the mixture of this body with water, consisted of $(SO_4CH_3)_2Ba$. The potassium salt was also prepared.

By acting in the same way on propyl, isobutyl, and amyl alcohols, the corresponding neutral sulphates were obtained, and from these the barium and potassium salts. The whole series of these ethers is more or less coloured. When they are distilled under ordinary pressure they undergo decomposition, but at 600 mm. oily drops were obtained from the ethyl compound identical in appearance with Wetherill's ether. The ether obtained from ethyl alcohol by means of sulphuryl oxychloride is the true neutral sulphate, that of Wetherill being the ether of oxethanesulphonic acid.

The change from one to the other on distillation may be explained by supposing diethyl sulphate to have the constitution—

$$C_2H_5O.SO_2.OC_2H_5,$$

so that the ethyl groups are not held by the same force, and therefore only one of them suffers decomposition. Which of the hydroxyl groups of sulphuric acid is more prone to suffer alteration is not decided, since the conversion of the ethyl sulphate into ethyl oxethanesulphonate may be expressed by either of the equations—

$$C_2H_5O.SO_2.OC_2H_5 = C_2H_4\begin{cases}OH\\SO_2\end{cases}OC_2H_5,$$

or

$$C_2H_5O\ O_2SOC_2H_5 = C_2H_4\begin{cases}OH\\O_2S\end{cases},OC_2H_5.$$

Oxethanesulphonic acid on the contrary has only one hydroxyl group united to oxygen, the second being directly united to carbon.

*Diphenyl sulphate* was obtained by the action of sulphuryl oxychloride on phenol, and resembles the compounds above described. The free acid was prepared from the lead salt corresponding with the potassium salt $(C_6H_5SO_4)K$.

*Nitrophenol sulphate*, from (volatile) mononitrophenol is another similar compound. The barium salt obtained by neutralising the acid product of decomposition of the body by water consisted of—

$$(C_6H_3NO_2SO_4)Ba + 2H_2O,$$

and is therefore identical with the salt obtained by Kolbe and by Armstrong from nitroxyphenolsulphuric acid—

$$C_6H_3NO_2\begin{cases}O\\SO_2\end{cases}Ba.$$

*Thymol sulphate* resembles the foregoing compounds.

Though the ethers of the aromatic series agree so closely with those of the $C_nH_{2n+1}$ series, they differ in their reaction with potassium sulphydrate. Not the slightest trace of phenyl-mercaptan was obtained by the action of the sulphydrate on phenol sulphate, nor on the potassium salt prepared by neutralising the product of decomposition by water. But possibly the reaction took place as follows :—

$$(C_6H_5)_2SO_4 + 2KHS + 2H_2O = 2H_2S + 2C_6H_5.OH + KO.SO_2.OK.$$

The potassium salt, $C_6H_5SO_4K$, is identical with that of paraphenolsulphonic acid (obtained by treating phenol with sulphuric acid), the constitution of which is—

$$C_6H_4\begin{cases}OH\\SO_2OK\end{cases}.$$

Therefore paraphenolsulphonic acid is among the products of decomposition by water of the body obtained by the action of sulphuryloxychloride on phenol. Similarly by the decomposition of the body pro-

duced by the action of sulphuryloxychloride on mononitrophenol by water, nitrophenolsulphonic acid was obtained, $C_6H_3NO_2\begin{cases}OH\\SO_2.OH\end{cases}$.

The bodies in question should therefore be regarded as the ethers of paraphenolsulphonic acid, the corresponding nitrophenolsulphonic acid, and an analogously constituted thymolsulphonic acid.

The following equations represent the decomposition of these three ethers by water:—

$$C_6H_4\begin{cases}OH\\SO_2.OC_6H_5\end{cases} + H_2O = C_6H_4\begin{cases}OH\\SO_2OH\end{cases} + C_6H_5OH.$$

$$C_6H_3NO_2\begin{cases}OH\\SO_2.OC_6H_4NO_2\end{cases} + H_2O = C_6H_3NO_2\begin{cases}OH\\SO_2OH\end{cases} + C_6H_4NO_2OH.$$

$$C_{10}H_{12}\begin{cases}OH\\SO_2.OC_{10}H_{13}\end{cases} + H_2O = C_{10}H_{12}\begin{cases}OH\\SO_2OH\end{cases} + C_{10}H_{13}OH.$$

If these experiments are conclusive as to the constitution of the compounds, they would show that the alcohols of the fatty series differ in their nature from the hydroxyl compounds of the homologues of phenyl, since by the action of sulphuryl oxychloride on the former true sulphuric ethers are produced, on the latter sulphonic ethers.

The supposition that the compound obtained from phenol might be identical with the isomeric oxysulphobenzide of Glutz (*Ann. Chem. Pharm.*, cxlvii, 52), prepared by heating phenol with sulphuric acid to 160°—

$$\left.\begin{matrix}C_6H_4OH\\C_6H_4OH\end{matrix}\right\}SO_2.$$

is shown by the properties of the two bodies to be unfounded.

G. T. A.

**Decomposition of Ethyl Acetate by Heat.** By A. Oppenheim and H. Precht (Deut. Chem. Ges. Ber., ix, 325).

Vapour of ethyl acetate passed through a tube heated to just below dull redness is resolved for the most part into acetic acid and ethene:

$$C_2H_3O.OC_2H_5 = C_2H_4O_2 + C_2H_4.$$

At a somewhat higher temperature acetone, carbon dioxide, and methane are also produced, owing to decomposition of the acetic acid first formed:—

$$CH_3.COOH = CH_4 + CO_2;$$
$$\text{and } 2CH_3.COOH = CH_3.CO.CH_3 + CO_2 + H_2O.$$

J. R.

**Preparation of Glycol.** By O. LIETZENMAYER (Liebig's Annalen, clxxx, 282—286).

THE author has examined the methods of preparing glycol proposed by Demole and by Zeller and Huefner.

Demole's process (which consists in boiling ethylene bromide and potassium acetate with alcohol) was found to yield some glycol monacetate, but no free glycol.

The Zeller-Huefner process gave better results, the yield of glycol being found to depend upon the proportion of water employed. The best result was obtained by boiling 50 grams of ethylene bromide and 40 grams of potassium carbonate with 160 grams of water for 18 hours in a flask provided with reversed condenser. The product gave by fractionation 8 grams of glycol.

J. R.

**Critical Observations on the new Dextrogyrate Amyl-alcohol of M. Belgues Bakhoven.** By J. A. LEBEL (Bull. Soc. Chim. [2], xxv, 199).

HAVING repeated Bakhoven's experiments with commercial amylic alcohol, the author is unable to discover any traces of the existence of the alcohol referred to, and considers it probable that the body in question was really a mixture of amylic ether, which is dextrogyrate, and the inactive alcohol.

C. H. P.

**Action of Electrolytic Oxygen on Glycerin.** By AD. RENARD (Compt. rend., lxxxii, 562—564).

GLYCERIN, mixed with two-thirds of its volume of dilute sulphuric acid (1 in 10), was electrolysed by a current from six Bunsen elements. At the negative pole hydrogen was evolved, and at the positive a mixture of 3 per cent. carbonic anhydride, 33 per cent. of carbonic oxide, and 64 per cent. of oxygen; after 48 hours calcium carbonate was added to the remaining liquid, which was then filtered and distilled. On spontaneous evaporation over sulphuric acid, a white amorphous residue of glyceric aldehyde, $C_3H_6O_3$, or more correctly, $(C_3H_6O_3)_4 H_2O$, remained.

Glyceric aldehyde is sparingly soluble in water and almost insoluble in alcohol or in ether. It melts at 71°—72° and boils at 130°—135°. It reduces ammoniacal silver nitrate, on oxidation it yields formic or acetic acids. When electrolysed it splits up into formic acid and carbonic anhydride and oxide.

The author was unable to convert it into glyceric acid, but with nascent hydrogen it appeared to be transformed into glycerin.

On treatment with sulphuretted hydrogen at 60°—80°, it deposits on cooling a gelatinous precipitate of the sulphaldehyde, $(C_3H_6S_2O)_2H_2O$. When dry this substance resembles wax; it softens at 80°—82° and boils at 180°—185°. It is soluble in hot and sparingly soluble in cold water, and insoluble in alcohol and in ether.

Glyceric aldehyde was treated with ammonia and the solution evaporated; crystals were deposited which, when purified by recrystallisation, had the composition $C_3H_6N_2$. They dissolved easily in water and in alcohol, but were insoluble in ether. When heated to 120°—130° it sublimed without previously melting in small brilliant crystals. When treated with hydrochloric or sulphuric acids it is reconverted into glyceric aldehyde; it is not altered on boiling with caustic soda.

The residue, after distillation of the aldehyde, gives on evaporation crystals of calcium formate, and on addition of ten times its volume of alcohol, deposits crystals of calcium acetate and glycerate. A glucose is also formed, owing to the polymerisation of the aldehyde, which evolves a smell of caramel when heated, and on oxidation yields oxalic acid. With baryta water it gives a flocky precipitate, with the formula of barium glucosate $(C_6H_{12}O_6)_4(BaO)_3 + 4H_2O$. It is not fermentable.

W. R.

**On Aldol.** By A. WURTZ (Bull. Soc. Chim. [2], xxiv, 100—101).

WHEN aldol-ammonia is distilled in a current of dry ammonia at 200°—300° water is formed, and an oily liquid passes over containing various basic substances; amongst these is one which forms a platinum salt crystallising in regular octahedrons, and having the composition of collidine chloroplatinate. The following equation represents the reaction:—

$$C_8H_{16}O_4 + NH_3 = C_8H_{11}N + 4H_2O.$$

The other bases have not yet been examined.

It is conceivable that, as aldol is formed from aldehyde, in a similar manner aldol might give rise to a substance, *dialdol*, having the constitution represented by the formula, $C_8H_{14}O_3$, or

$$CH_3.CH(OH).CH_2.CH(OH).CH_2.CH(OH).CH_2.CHO.$$

This compound, which is both a trihydric alcohol and an aldehyde, has not been isolated, but its first anhydride has been obtained and studied. This substance, *dialdane*,

$$CH_3.CH(OH).CH_2.CH{=}CH.CH(OH).CH_2.CHO,$$

is formed from dialdol by the elimination of a molecule of water, and bears the same relation to aldol that crotonic aldehyde does to aldehyde. Dialdane fuses at 139° and distils at 137° under a pressure of 2 centimetres of mercury. It dissolves in boiling water, but crystallises out in great part on cooling in brilliant scales. It is very soluble in alcohol, but only slightly so in ether. Its aqueous solution reduces silver oxide with formation of a mirror, giving rise to a monobasic acid, $C_8H_{14}O_4$, the silver, sodium, barium, and calcium salts of which are crystalline. It is formed from dialdane by the transformation of the aldehyde group, CHO, into carboxyl, COOH. It is very acid, and distils at 198° under a pressure of 2 centimeters of mercury.

It is soluble in alcohol and in water, separating from its hot aqueous solution in magnificent clinorhombic crystals which fuse at 80°.

C. E. G.

## The Residue in the preparation of Chloral. By C. FRIEDEL (Chem. Centr., 1875, 514).

ON an examination of this residue, *pentachloracetal*,

$$CCl_3—CH\left\{\begin{matrix} OC_2H_3Cl_2 \\ OC_2H_5 \end{matrix}\right.,$$

was found. It forms a colourless fluid, boiling at 186°—189°. Solution of potash has no action upon it, but on heating with solid potash it loses one molecule of hydrochloric acid, forming $CCl_2{=}C\left\{\begin{matrix} OC_2H_3Cl_2 \\ OC_2H_5 \end{matrix}\right.$, a colourless liquid, boiling at 153°—159°. Sulphuric acid converts *pentachloracetal* into chloral and products not yet examined.

H. H. B. S.

## Amides of Chloral. By C. O. CECH (Deut. Chem. Ges. Ber., ix, 437—340).

CHLORAL cyanide-cyanate, $C_4H_3Cl_3N_2O_2$, a body previously described by the author (see this Journal, 1876, 376), combines directly with aniline when dissolved therein, with great rise of temperature and evolution of hydrocyanic acid. The product dissolves sparingly in water and easily in ether, alcohol, carbon bisulphide, and glacial acetic acid, and crystallises from the solutions in needles. From a mixture of ether and alcohol it crystallises in large colourless tables, which turn rose-red in the air. It melts at 117°. When heated it emits the characteristic odour of phenyl cyanate, but sublimes partly undecomposed in long silky needles. Hot acids dissolve it, forming solutions from which it crystallises in needles on addition of water; boiling alkalis convert it into isonitril. The substance gave on analysis numbers agreeing with the formula, $C_8H_7Cl_2NO$. From this the author deduces the constitutional formula—

$$\begin{matrix} CCl_2—N\begin{matrix} C_6H_5 \\ H \end{matrix} \\ | \\ HC{=}O \end{matrix} \quad \text{or} \quad N\left\{\begin{matrix} C_6H_5 \\ H \\ (C_2HCl_2O) \end{matrix}\right.,$$

according to which the substance is *chloralmonanilide*, the first-known amide of chloral. Its formation is represented by the equation—

$$C_4H_3Cl_3N_2O_2 + C_6H_7N + H_2O = C_{10}H_{12}Cl_3N_3O_3 = C_8H_7Cl_2NO + CO_2 + CHN + H_4ClN.$$

Chloralanilide is formed also when aniline hydrochloride is added to a mixture of chloral hydrate and potassium cyanide and cyanate.

J. R.

**Hydrogenation of Ethyl-propyl Ketone.** By W. OECHSNER (Bull. Soc. Chim. [2], xxiv, 99).

THE ketone employed for this purpose was prepared by carefully fractionating the product of the distillation of calcium butyrate. It boiled at 122°—124°, and had a specific gravity of ·833 at 0°. When acted on by sodium in presence of water, according to the method adopted by Friedel, it gives a secondary hexylic alcohol, $C_6H_{14}O$, or $(C_2H_5)(C_3H_7)CH.OH$, and a pinacone, $C_{12}H_{26}O_2$. The former is a colourless mobile liquid boiling at about 135°; the latter an oily liquid, of a slightly camphorous odour, distilling at about 255°, which is converted into a pinacoline with loss of a molecule of water when treated with dilute sulphuric acid.

C. E. G.

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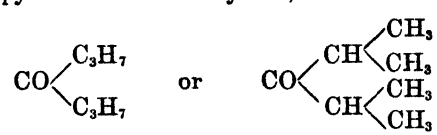
**Dipseudopropyl Ketone and Methyl-pseudopropyl Ketone.** By R. MÜNCH (Liebig's Annalen, clxxx, 327—342).

DIPSEUDOPROPYL ketone was obtained by oxidising isobutyl alcohol with potassium bichromate and sulphuric acid, neutralising the isobutyric acid thus formed with milk of lime, and distilling the calcium salt in a steel tube. The crude product was a brown, highly refractive liquid which yielded by fractional distillation a portion boiling at 124°—126°, and having the composition of the ketone of isobutyric acid.

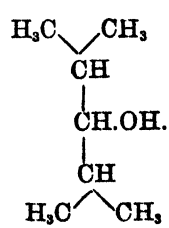
Dipseudopropyl ketone or isobutyrone,



forms a clear, mobile, highly refractive liquid of ethereal camphor-like odour, freely soluble in alcohol and ether, but insoluble in water. It is readily inflammable and burns with a smoky flame. Sp. gr. 0·8254 at 17°. It reduces an ammoniacal solution of silver, but does not combine with bisulphites of the alkalis. When boiled with a solution of chromic acid it yields isobutyric and acetic acids and carbon dioxide, the oxidation probably taking place as represented by the equation—

$$C_7H_{14}O + O_6 = C_4H_8O_2 + C_2H_4O_2 + CO_2 + H_2O.$$

Sodium-amalgam acting on the ketone dissolved in benzene converts it into a secondary heptyl alcohol and a pinacone. The former of these products, from its mode of formation, must have the constitutional formula—



It is a colourless liquid of agreeable ethereal peppermint-like odour and burning taste, sparingly soluble in water and easily in alcohol and ether. Sp. gr. 0·8323 at 17°; boiling-point 131°—132°. By cautious treatment with chromic acid it is re-converted into isobutyrone.

Methyl-pseudoproyl ketone, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH—CO—CH_3$, was obtained by distilling a mixture of calcium isobutyrate and acetate in a steel tube and fractionating the dark-brown distillate. It is a mobile, colourless, highly refractive liquid of ethereal odour, easily soluble in alcohol and ether, boiling at 93°—94°. Sp. gr. 0·815 at 15°. It does not reduce ammoniacal silver nitrate. Sodium bisulphite forms with it a white crystalline compound, from which the ketone is liberated unchanged by alkaline carbonates. Chromic acid in strong solution, when boiled with the ketone, oxidises it to acetic acid, carbon dioxide, and water. Nascent hydrogen converts it into a secondary amyl alcohol* boiling at 108°, of agreeable ethereal odour and burning taste, easily soluble in alcohol and ether, of sp. gr. 0·827 at 17°, and yielding by oxidation with chromic acid the ketone from which it is derived. Together with this alcohol there is formed a high-boiling product resembling the pinacone formed from isobutyrone under the same circumstances.

The isobutyl isobutyrate obtained in the preparation of isobutyric acid, when heated to 170° with a mixture of aqueous and alcoholic ammonia in sealed tubes, yielded isobutyramide, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH—CONH_2$, a body crystallising in thin shining scales, very soluble in water and alcohol and melting at 124·5°.

J. R.

## Synthesis of Organic Acids by means of Carbon Oxychloride.

By W. Michler (Deut. Chem. Ges. Ber., ix, 400—402).

When carbon oxychloride, liquefied in a freezing mixture, is mixed with dimethylaniline, the two bodies react upon each other in the manner indicated by the equation—

$$2N\begin{matrix}C_6H_5\\(CH_3)_2\end{matrix} + COCl_2 = HClN\begin{matrix}(CH_3)_2\\C_6H_5\end{matrix} + \begin{matrix}CH_3\\NCH_3\\C_6H_4COCl\end{matrix}.$$

The last product, when treated with water, yields dimethyl-amidobenzoic acid, $N(CH_3)_2C_6H_4COOH$, melting at 235°, and identical with that obtained by the action of methyl iodide on para-amidobenzoic acid.

J. R.

* In the analysis of this substance, 0·120 gram furnished 0·284 gram carbon dioxide, and 0·147 gram water. The formula deducible from these numbers is $C_4H_{10}O$; not $C_5H_{12}O$, as stated by the author.—J. R.

**Formation of Ethyl-diacetic Acid and Oxyuvitic Acid.** By A. OPPENHEIM and H. PRECHT (Deut. Chem. Ges. Ber., ix, 318—323).

ETHYL-DIACETIC acid is conveniently prepared in large quantity by a slight modification of Geuther's process, viz., by dissolving sodium in ten times its weight of ethyl acetate and adding the crude product whilst warm to the necessary quantity of glacial acetic acid diluted with four times its bulk of water. A mixture of ethyl acetate and ethyl-diacetic acid rises to the surface of the sodium acetate solution thereby formed, and may be separated by fractional distillation. The product boils at 180°—181°, and corresponds exactly with Geuther's description. Its vapour-density was found to be 65·15, the formula, $C_6H_{10}O_3$, requiring the density 65.

Pure and dry ethyl acetate dissolves sodium very slowly at first without evolving hydrogen, but when once begun the action proceeds with increasing rapidity, because sodium ethylate is formed which reacts with ethyl acetate to form the sodium salt of ethyl-diacetic acid. Still, however, no hydrogen is evolved. The reaction is supposed by the authors to proceed in the manner indicated by the following equations:—

$$CH_3.CO.OC_2H_5 + Na = NaOC_2H_5 + CH_3CO;$$

$$CH_3.CO + CH_3.CO.OC_2H_5 + Na = \underbrace{CH_3.CO.CHNa.COOC_2H_5}_{\text{Sodium ethyl-diacetate.}} + H_2;$$

$$H_2 + Na_2 + CH_3.CO.OC_2H_5 = CH_3CH_2.ONa + NaOC_2H_5;$$

according to which 1 part of sodium should produce 1·41 part of ethyl-diacetic acid: experimentally 1·5 parts were formed.

Direct experiments on the conditions under which oxyuvitic acid is produced showed that it is not formed by the action of chloroform on the sodium salt of ethyl-diacetic acid alone, but that the presence of sodium alcoholate is also necessary. The reaction of chloroform on sodium ethyl-diacetate alone results in the formation of a crystallisable acid substance which is not yet investigated.

J. R.

**Preparation and Properties of Dehydracetic Acid.** By A. OPPENHEIM and H. PRECHT (Deut. Chem. Ges. Ber., ix, 323—325).

THE authors, after endeavouring unsuccessfully to prepare this substance in quantity by heating ethyl-diacetic acid in open vessels and in sealed tubes, and by treating it with zinc chloride and hydrochloric acid, hit upon the expedient of passing the vapour through a heated tube, which proved perfectly successful. Ethyl-diacetic acid was distilled from a flask connected with one end of an iron tube filled with fragments of pumice, and having at the other end a receiver and condenser. The tube was heated to just below dull redness, that being

found to be the most favourable temperature. In this way 900 grams of the acid yielded 212 grams ( = 23·5 per cent.) of pure dehydracetic acid.

The properties of the acid were found to agree with Geuther's description. It melts at 108·5°, and boils at 269°, being partially decomposed by boiling. With ferric chloride it gives a yellow to orange colour. It is extremely stable in presence of strong acids, crystallising unaltered, on cooling, from its solutions in boiling strong hydrochloric and nitric acids. It is taken up by ether from its solution in hot strong sulphuric acid. Alkalis, on the contrary, decompose it very easily. When heated with excess of strong soda-ley it froths violently, owing to the sudden formation of acetone: the residue contains sodium carbonate and acetate. The decomposition is represented thus:

$$C_8H_8O_4 + 3H_2O = 2C_2H_4O_2 + C_3H_6O + CO_2.$$

When heated to 160° with baryta- or lime-water, in sealed tubes, the acid undergoes for the most part a similar decomposition. A portion, however, is decomposed in a different manner, apparently with formation of orcin or a similar body.

The methyl-ether of dehydracetic acid forms yellow four-sided prisms, melting at 91°.

J. R.

**Sulphur-compounds of Pyroracemic Acid.** By C. Bottinger (Deut. Chem. Ges. Ber., ix, 404).

Pyroracemic acid forms with silver oxide a salt which, when decomposed with hydrogen sulphide, yields an acid agreeing approximately with the formula $C_3H_4SO_2$.

Hydrogen sulphide passed into pyroracemic acid forms with it a solid compound, which is decomposed by water. Its composition agrees with the formula $C_6H_8SO_5 = C_3H_4O_3 + C_3H_4O_2S$. It begins to melt at 87°, undergoing decomposition.

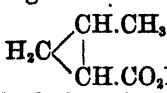
J. R.

**The Dibromide of Angelic Acid.** By E. Demarçay (Compt. rend., lxxx, 1400—1402).

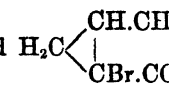
When this compound is distilled, it evolves a large amount of gas, and an oil passes over which sometimes crystallises; on dissolving this oil in potash, boiling the solution, after separating a small quantity of a brominated liquid, and adding excess of sulphuric acid, an oil separates which soon solidifies to a crystalline mass. These crystals, after being purified by distillation and pressure, melt at 61°—62°. They have an odour recalling that of angelic acid, and are but moderately soluble even in boiling water, crystallising out on cooling in small lustrous needles. It boils at about 196°, and its ethylic ether, the odour of which closely resembles that of ethyl angelate, boils at 153°—155°. It is isomeric with angelic acid, $C_5H_8O_2$, and unites directly with a molecule of bromine to form the compound $C_5H_8Br_2O_2$. It will be seen, there-

fore, that it closely resembles Frankland's methylcrotonic acid, and as it yields acetic and propionic acids when fused with potash, there can be little doubt that they are identical.

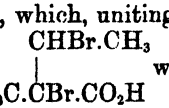
The author finds that the bromides of methylcrotonic acid and of angelic acid are identical, so that either bromine in acting on angelic acid gives the dibromide of its isomeride, or, what is very unlikely, considering the formula of methylcrotonic acid, the dibromide of angelic acid is produced by the action of bromine on methylcrotonic acid. If we admit Frankland's hypothesis that angelic acid is propylenated acetic acid, the reaction is easily explained. The action of bromine on angelic acid—



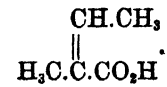

gives rise to bromangelic acid




and hydrobromic acid, which, uniting at the instant of formation, produce the compound




which is the dibromide of methylcrotonic acid, methylcrotonic acid being

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C. E. G.

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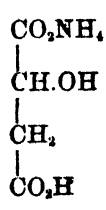
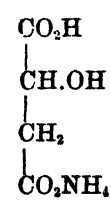
**The Active Malic Acids.** By G. J. W. BREMER (Bull. Soc. Chim. [2], xxv, 6).

THE malic acid obtained by the action of hydriodic acid on dextro-tartaric acid has the rotatory power + 3·157°, while that of ordinary malic acid from the mountain ash is − 3·299°. This explains why, by the reduction of racemic acid, an inactive malic acid is obtained. The acid ammonium salts of the two active acids turn + 7·912° and 5·939°. But when the acid calcium salt of levomalic acid is neutralised by ammonia and the calcium removed by oxalic acid, the acid ammonium salt thus obtained turns − 7·816°. This salt, therefore, exists in two isomeric forms, having the constitution:




C. S.

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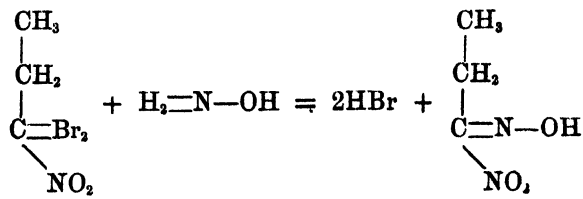
**Synthesis of Propylnitrolic Acid.** By V. MEYER and M. LECCO (Deut. Chem. Ges. Ber., ix, 395—396).

THE authors have previously shown that ethylnitrolic acid is formed by the action of hydroxylamine on dibromonitroethane (see this Journal, 1875, 57). The same reaction has now been extended to the propyl

series. Propylnitrolic acid is formed by adding dibromonitropropane (prepared from primary nitropropane) to hydroxylamine hydrochloride mixed with an equivalent quantity of barium hydrate, and allowing the mixture to stand for two days. When pure it crystallises in long light-yellow prisms melting at 60° and having all the properties of the substance formed by the action of nitrous acid on nitropropane. The reaction is represented by the equation:



J. R.

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**Researches on Taurine.** By R. ENGEL (Compt. rend., lxxx, 1398—1400).

TAURINE, generally considered as isethionamide, is in reality a glycocine, that is an acid amide, and has been prepared synthetically by the action of ammonia on chlorethylsulphurous acid. The isethionamide of Strecker differs from taurine in its fusion point, and moreover, evolves ammonia when boiled with a solution of potassium hydrate. The glycocines unite with cyanic acid, giving uramic acids, of which hydantoic acid is the type; and in a similar way taurine yields taurocarbamic acid, a substance analogous to the hydantoic acids. From these circumstances it seemed likely that taurine should yield salts similar to those obtained from the glycocines, and also that it should unite with cyanamide to form a compound analogous to creatine.

In fact when a solution of taurine is heated with an excess of recently precipitated mercuric oxide, the yellow colour of the latter disappears, and a white precipitate of a basic salt of taurine is obtained, having the composition $\left(\begin{matrix}CH_2NH_2\\CH_2OSO_2\end{matrix}\right)_2Hg + HgO$. As it is insoluble in water and but slightly soluble in dilute acetic acid, there is no difficulty in removing the excess of mercuric oxide. On adding a solution of potassium hydrate to a solution of mercuric chloride mixed with an excess of taurine, no precipitate is obtained. It is possible that a soluble compound $\left(\begin{matrix}CH_2NH_2\\CH_2OSO_2\end{matrix}\right)_2Hg$ is formed in this case.

On allowing a solution of taurine with excess of cyanimide to stand for three months, and then evaporating, crystals of dicyanamide were first obtained, and then a white substance insoluble in boiling alcohol. On adding silver nitrate to its aqueous solution, and then potassium hydrate, a white precipitate is obtained, just as with creatine; on gently heating, the silver is reduced. The author has not as yet examined this new compound.

C. E. G.

**A New Method for Preparing Thio-ureas.** By P. MIGUEL (Bull. Soc. Chim. [2], xxv, 104—106).

WHEN dry ammonia is passed into a solution of acetyl sulphocyanate in dry ammonia, an oil separates out consisting of *acetylthio-urea* $CS\left\{\begin{matrix}NH_2\\NH.C_2H_3O\end{matrix}\right.$. It is a thick, heavy, yellow liquid, having a faint and insipid smell; it is decomposed by water and insoluble in ether and carbon sulphide. When heated it decomposes into ammonia, hydrogen sulphide, ammonium sulphhydrate and acetamide. Aqueous ammonia resolves acetyl sulphocyanate into acetate and sulphocyanate of ammonium.

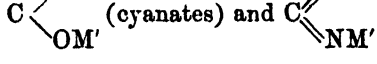
When benzoyl sulphocyanate is treated with aqueous or dry ammonia, it is at once converted into benzoyl-urea, crystallising in prisms melting at 171° and having an exceedingly bitter taste. It is soluble in alcohol and very sparingly in hot water, and much less so in ether and carbon sulphide.

By the action of benzylamine on benzoyl sulphocyanate, the compound $CS\left\{\begin{matrix}NH_2\\N(C_7H_7)C_7H_5O\end{matrix}\right.$ is obtained in flexible, silky needles melting at 130°.

C. S.

**On Cyanic Acid Compounds.** By ANTON FLEISCHER (Deut. Chem. Ges. Ber., ix, 436—440).

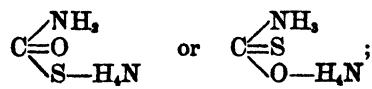
OF the two possible series of metallic cyanates—



one only is as yet known, and it is still doubtful to which series the known cyanates belong. In the ethers of cyanic acid alone are both series represented.

A recent experiment of the author's seems to throw some light on this subject.

Ammonium oxysulphocarbamate may be represented by either of the formulæ—



but it has previously been shown, by the experiments of Berthelot and Kretschmar, and also by the author in conjunction with Steiner, that this salt, when deprived of the elements of hydrogen sulphide, yields carbamide; and the author has now arrived at the same result by treating the salt with mercuric oxide at low temperatures, whereby he obtained 80 p. c. of the theoretical amount of carbamide. Whence it is concluded that the true formula of ammonium oxysulphocarbamate is that containing the group CO. The formation of carbamide by

abstraction of hydrogen sulphide must, therefore, be represented thus:—

$$CO\begin{cases}NH_2\\SH_4N\end{cases} - H_2S = CON_2H_4.$$

This process may take place in either of the ways indicated by the following diagrams:—

$$CO\begin{cases}NH_2\\SH_2\,H_4N\end{cases};\quad CO\begin{cases}N\,H\\S\,H_4N\end{cases}.$$

Now, the liquid obtained by the action of mercuric oxide on ammonium oxysulphocarbamate contains an ammonium salt, which effervesces with acids and gives with silver, lead, and other salts, precipitates containing nitrogen and free from hydrogen. This ammonium-salt, which yields carbamide when evaporated, can only be ammonium isocyanate, constituted according to the formula $C\begin{cases}N—NH_4\\O\end{cases}$; and the other salts must consequently be isocyanates, having the general formula CONM′.

The author is continuing his investigations.

J. R.

## Remarks on Fleischer's "Mercury Oxysulphocyanate." By J. Philipp (Liebig's Annalen, clxxx, 341—342).

Referring to a recent paper by Fleischer, in which he describes as a basic mercuric sulphocyanate a yellow body obtained by adding ammonia to a solution of mercury sulphocyanate in ammonium sulphocyanate, the author points out that he described the same body some years ago (*Pogg. Ann.*, 131, 86), but arrived at a different conclusion as to its constitution. Fleischer assigns to the body the formula $Hg(CNS)_2 + 3HgO$. Philipp, however, regards it as mercurammonium oxysulphocyanate, $N(HgH_2)CNS + HgO$, which view accords better with the composition and properties of the body.

J. R.

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## On Ethyl Oxalurate. By F. Salomon (Deut. Chem. Ges. Ber., ix, 374—379).

This body has been previously obtained by Henry by the action of ethyloxalic chloride on urea, and by Grimaux by the action of silver oxalurate on ethyl iodide. The statements of these chemists respecting it not being quite concordant, the author has examined afresh the substances formed in both processes.

1. *From Silver Oxalurate.*—The ether is conveniently obtained by boiling this body with a slight excess of ethyl iodide or bromide in absolute alcohol, filtering the solution while hot, and exhausting the residue with boiling alcohol, which deposits the ether, on cooling, in

the form of a white powder. By crystallisation from boiling ether, the compound is obtained in delicate white silky needles, melting at 177°—178°.

A solution of the ether in hot water gives, on adding to it one drop of ammonia and then silver nitrate, a gelatinous precipitate of silver parabanate, $C_3N_2Ag_2O_3,H_2O$. Baryta-water, added to a hot solution of the ether, produces a crystalline precipitate of barium oxalate, whilst urea remains in solution; the reaction is represented thus:—

$$\begin{matrix} NHCONH_2 \\ COCOOC_2H_5 \end{matrix} + Ba\begin{matrix} OH \\ OH \end{matrix} = \begin{matrix} COO \\ COO \end{matrix}Ba + CO\begin{matrix} NH_2 \\ NH_2 \end{matrix} + C_2H_5OH.$$

When the ether is heated to 120° with alcoholic ammonia, the solution deposits, as it cools, a crystalline powder, together with short needles; and on evaporating the liquid, long needles of an easily soluble body (urea?) crystallise out. The solid substance dissolves easily in strong sulphuric acid without decomposition: on diluting the solution, it deposits a crystalline powder, consisting of pure oxalan.

On attempting to crystallise ethyl oxalurate from hot water, the solution acquires an acid reaction, and leaves, on evaporation, a white crystalline mass, having a strongly acid reaction and melting at 155°. The same body is formed when the ether is evaporated with dilute hydrochloric acid. It consists of a mixture of oxalic acid and oxalate of urea.

2. *From Urea and Ethyloxalic Chloride*.—The ethyl oxalurate obtained by the reaction of these substances, in the manner described by Henry, behaved towards silver nitrate, baryta-water, ammonia, and dilute acids, in the same way as that prepared from silver oxalurate. The author thinks there can be no doubt of the identity of the two preparations.

The reaction of ethyl oxalurate with silver solution to form silver parabanate, shows that oxaluric acid stands in the same relation to parabanic acid as urea to cyanic acid.

J. R.

## On Methyluric Acid. By H. Hill (Deut. Chem. Ges. Ber., ix, 370—372).

This substance, $C_5H_3(CH_3)N_4O_3$, is obtained by heating dry lead urate to 150°—160° with methyl iodide diluted with ether, and treating the product with hydrogen sulphide to remove lead. The hot filtrate, on cooling, deposits crystals of the new body, which are purified by dissolving them in hot soda-ley, precipitating with hydrochloric acid, and recrystallising from boiling water. It forms thin prisms, fusible with decomposition at a high temperature, soluble in 250 parts of boiling water, nearly insoluble in alcohol and ether. The aqueous solution reddens litmus. The ether dissolves in cold strong sulphuric acid, and is deposited in crystals when the solution is diluted. It dissolves easily in alkalis: alcohol throws down from the solutions dense precipitates of the alkali-salts, aqueous solutions of which precipitate many salts of the metals.

When methyluric acid is heated to 170° with *hydrochloric acid*, the products are carbon dioxide, methylamine, ammonia, and glycocine.

J. R.

## On Aromatic Compounds which prevent the Precipitation of Cupric Hydrate by Alkalis. By W. Weith (Deut. Chem. Ges. Ber., ix, 342—343).

According to the experiments of Wislicenus and Coray, certain oxy-acids and polyatomic alcohols of the fatty series possess the above-named property, which, in the case of the oxy-acids, is due to the circumstance that after the hydrogen of the carboxyl has been replaced by sodium, the hydrogen of the hydroxyl becomes replaceable by copper, and thus easily-soluble double compounds are formed. Weith finds that amongst bodies of the aromatic series, only ortho-compounds prevent the precipitation of copper sulphate by alkalis. Salicylic acid mixed with copper sulphate and soda-ley, forms a dark bluish-green solution, from which no trace of copper hydrate is thrown down by a large excess of alkali. One mol. of salicylic acid, with at least two mol. of sodium hydrate, prevents the precipitation of half a molecule of copper sulphate. One mol. of the acid, with only one mol. of soda, gives, with copper sulphate, a precipitate of ordinary copper salicylate, which dissolves readily in excess of soda. Oxybenzoic and para-oxybenzoic acids, on the contrary, do not prevent the precipitation.

Similarly with the dioxybenzenes. Pyrocatechin, with excess of soda, retains a large quantity of copper in solution; resorcin and hydroquinone have no such effect. As might be expected, gallic, pyrogallic, and quinic acids do not prevent the precipitation.

The aromatic dibasic acids which are not oxy-acids (phthalic, isophthalic), and the univalent hydroxyl-compounds (phenol, orthocresol), when mixed with copper sulphate and excess of soda, do not form solutions containing copper.

Weith thinks that the behaviour of aromatic compounds towards copper sulphate and alkalis may serve as a means of determining whether the carboxyl- and hydroxyl-groups in them occupy the ortho-position.

J. R.

## Trinitrobenzene. By Paul Hepp (Deut. Chem. Ges. Ber., ix, 402).

This substance is formed by heating metadinitrobenzene with a mixture of fuming sulphuric and strong nitric acids. It crystallises from alcohol in white laminæ or needles, melting at 121°—122°, and subliming readily. Dissolves also in ether, and sparingly in boiling water. Analysis agrees with the formula $C_6H_3(NO_2)_3$.

J. R.

**On the Trimethylbenzenes of Coal-tar Oil, and their Separation.** By OSCAR JACOBSEN (Deut. Chem. Ges. Ber., ix, 256—258).

To separate the two trimethylbenzenes, the author first prepares the amides of their sulpho-acids. From a mixture of the sodium salts of the sulpho-acids, the acid chlorides are prepared by means of phosphorus pentachloride, and from these the amides by means of ammonia. The amides can then be easily separated by crystallisation from alcohol. Mesitylene-sulphamide, when crystallised from alcohol, forms a soft, fibrous, asbestos-like mass. From a hot aqueous solution it is deposited on cooling in very long, capillary needles. It is very easily soluble in alcohol, less so in ether, and almost insoluble in cold water. It melts at 141° to 142°.

Pseudocumenesulphamide is far less soluble in alcohol, and separates on cooling or evaporation of the liquid in hard, transparent, short, prismatic crystals. It melts at 175°—176°. Both amides can be boiled for a long time with water without suffering decomposition. They are decomposed by concentrated hydrochloric acid only at a temperature at which the sulpho-acids are split up into sulphuric acid and the hydrocarbons. These hydrocarbons were, therefore, prepared by heating the amides for a short time with fuming hydrochloric acid to 170°—175°. If the mesitylene is neglected, the greater part of the pseudocumene may be extracted from the coal-tar oil in a much simpler manner.

Pseudocumene-sulphuric acid crystallises with water in obtuse rhombohedrons, which are relatively little soluble in dilute sulphuric acid. If, therefore, the solution of the mixed hydrocarbons in sulphuric acid is mixed with the proper amount of water, the pseudocumene-sulphuric acid can be separated by repeated crystallisation so perfectly, that no trace of mesitylene can be detected in the hydrocarbon prepared from it through the trinitro-derivative.

G. T. A.

**Fluorene and its Alcohol.** By P. BARBIER (Compt rend., lxxx, 1396—1397).

AFTER alluding to a previous communication in which he described the transformation of fluorene, $C_{12}H_8.CH_2$ into diphenylene-carbonyl, $C_{12}H_8.CO$, showing that the latter compound and diphenyl-formic acid, $C_{12}H_8.CH_2O_2$, might be considered as derivatives of fluorene, he proceeds to describe some new compounds obtained from diphenylene-carbonyl.

*Fluorenic Alcohol*, $C_{13}H_9.OH$.—This substance is obtained by the action of sodium amalgam on diphenylene-carbonyl in alcoholic solution. After being purified by crystallisation from boiling benzene, it forms hexagonal plates which melt at 153°. Treatment with chromic acid reconverts it into diphenylene-carbonyl.

*Fluorenic Ether*, $(C_{13}H_9)_2O$.—When the alcohol is heated for some time above its fusing point, it loses water, and is converted into a

resinous substance, melting at about 290°. It is also formed when the alcohol is heated with glacial acetic acid to 150°—160°.

*Fluorenic Acetate*, $C_{13}H_9.C_2H_3O_2$.—This compound is formed when fluorenic alcohol is heated with glacial acetic acid at 100° for eight hours. It crystallises in rhomboïdal plates, which melt at 75°. Heated to 150° with baryta-water, it gives barium acetate.

C. E. G.

## Normal Phenyl-ethyl Alcohol. By B. Radziszewski (Deut. Chem. Ges. Ber., ix, 372—373).

This substance was obtained by treating the aldehyde of phenylacetic acid with sodium amalgam. The aldehyde itself was obtained by distilling a mixture of calcium phenylacetate and calcium formate. It is a colourless oily liquid of sp. gr. 1·085, boiling at 205°—207°, having a pungent, characteristic odour, and forming, with acid sodium sulphite, a compound, ($C_8H_8O.NaHSO_3 + H_2O$), which crystallises in white shining laminæ. This aldehyde, when acted on with sodium amalgam, yields normal phenyl-ethyl alcohol, $C_6H_5CH_2CH_2OH$,—a colourless liquid of sp. gr. 1·033, boiling at 212°. The latter, by oxidation with chromic acid, is converted into phenylacetic acid, melting at 76·5°.

The acetic ether of this alcohol, $C_6H_5CH_2CH_2O—C_2H_3O$, is easily obtained by heating it to 150° with acetic anhydride. It is a colourless liquid, of strong agreeable odour, boiling at 224°. Sp. gr. 1·0286.

J. R.

## The Terpene of Parsley Oil. By E. v. Gerichten (Deut. Chem. Ges. Ber., ix, 258—260).

The parsley oil used began to boil at 160°, and all the terpene had passed over at 210°. The thermometer then rose rapidly, and other products were obtained which the author is investigating. By repeated rectification a colourless terpene boiling at 160°—164°, and with an intense smell of parsley, was obtained. The vapour-density of this body was taken in vapour of oil of turpentine, and gave 67·62 instead of 68·00. Its sp. gr. at 12° was 0·865. The left handed rotation for yellow light for a layer 100 mm. thick was −30·8 (Wild's instrument).

By long contact with concentrated hydrochloric acid, the colour of the terpene becomes brown, and it loses its intense parsley-smell, but does not form crystals of a hydrochloride. No terpin could be obtained. The terpene saturated with hydrochloric acid did not deposit a solid hydrochloride after standing for a day in winter, but on being poured out on a broad surface and diluted with alcohol, a small quantity was obtained which had a camphor-like smell and melted at 115°—116°.

By treatment with iodine a hydrocarbon was obtained, the boiling point of which could not be determined, but which gave oxidation-products (paratoluic acid, m.p. 173°—176°, and terephthalic acid) pointing to paracumene.

Further accounts of the products obtained from parsley seeds will be published shortly.

G. T. A.

## The Isomeric Camphors and Borneols.

By J. DE MONGOLFIER (Bull. Soc. Chim. [2], xxv, 17—19).

THE borneol which the author obtained together with camphic acid by the action of alcoholic potash on camphor, has the rotatory power 9·6° for the D line, while Berthelot found 44° and Kachler 42° for the product prepared by Baubigny's process; but Riban found it only to be 2·6°, and the author in one case 1·5°, and in another in which a high temperature was used, 29·5°.

Similar results are obtained by using rosemary-camphor, from which it appears that the different borneols are mixtures of an active and an inactive modification which readily change into each other.

C. S.

## On the Products of Reduction, and the Composition of Anethol.

By F. LANDOLPH (Compt. rend., lxxxii, 849—852).

IN order to obtain the hydrocarbons corresponding with the chief radicals in this body, the author heated it with amorphous phosphorus and hydriodic acid of sp. gr. 1·72 to 260° for 24 hours (3 parts anethol, 2 of phosphorus, and 25 of hydriodic acid). In this way, from 80 grams of pure crystallisable anethol distilling at 228°—230°, there were obtained 40 of a hydrocarbon distilling at 60°—250°, and 10 passing over at above 300°, after washing with dilute sulphur dioxide solution to separate free iodine. By fractional distillation an octane and a hydrocarbon of composition $C_{12}H_{22}$ were separated from the former portion, boiling respectively at near 150° and 210°—212°, after separation of traces of benzene by means of cold fuming nitric acid, and reduction of the resulting nitro-compounds by means of tin and hydrochloric acid. The octane possessed the vapour density 4·01; 3·92; 3·81; mean = 3·91, calculated 3·87, whilst the other hydrocarbon gave the numbers 5·66; 5·73: mean = 5·70; calculated 5·73, these values being obtained in aniline and anethol vapours respectively by means of Hofmann's apparatus.

The unsaturated hydrocarbon, $C_{12}H_{22}$, combined directly with bromine, and was present to the extent of rather more than one-third of the total hydrocarbons formed during the reduction, the octane forming about one-third: the gas liberated was almost pure hydrogen, containing not more than two or three per cent. of a hydrocarbon, probably benzene and hexylene, or possibly ethane or methane.

Hence the chief action of hydriodic acid on anethol is represented by the equation—

$$2C_{10}H_{12}O + 9H_2 = C_6H_{16} + C_{12}H_{22} + 2H_2O,$$

Hence the author concludes that the formula of anethol should be doubled (notwithstanding its vapour density which corresponds with

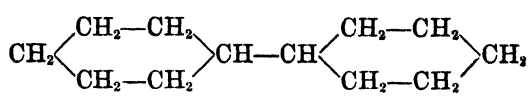
the $C_{10}$ formula), and that the body may be regarded as formed from a hypothetical aldehyde (termed by him acecampholic aldehyde), $C_{12}H_{16}O$, which is itself derived from the unknown acetylene oxide, $C_2H_2O$, and campholic aldehyde, $C_{10}H_{16}O$, by elimination of $H_2O$. By union with anisic alcohol, $C_8H_{10}O_2$ and elimination of $H_2O$, this hypothetical acecampholic aldehyde gives rise to anethol, thus—

$$C_8H_{10}O_2 + C_{12}H_{16}O = H_2O + C_{20}H_{24}O_2.$$

Anethol is thus regarded as a kind of acetal: this view of its constitution is in harmony with the author's previous results, whereby it was shown that on oxidising anethol by nitric acid, there are obtained equal quantities of anisic aldehyde, $C_8H_8O_2$, and anisic camphor, $C_{10}H_{10}O$, with a certain amount of acetic acid; *i.e.*, it is made up of a $C_8$, a $C_{10}$, and a $C_2$ compound.

C. R. A. W.

*Note by Abstractor.*—It would seem possible that the formation of a $C_{12}$ hydrocarbon from a $C_{10}$ benzene derivative might take place by the coalescence of two benzene groups, and the formation of a hydrocarbon, $C_{12}H_{22}$, having the structure—



this body might perhaps be obtained by hydrogenising diphenyl by means of hydriodic acid and phosphorus.

C. R. A. W.

## Action of Iodine and Mercuric Oxide on Anthracene.

By O. Zeidler (Chem. Centr., 1875, 740).

The materials were heated together in a vessel fitted with an upright condenser, the anthracene being dissolved in hot alcohol.

Anthraquinone was produced: 70 per cent. of the amount theoretically obtainable according to the equation—

$$C_{14}H_{10} + 2HgO + 3I_2 = C_{14}H_8O_2 + 2HgI_2 + 2HI$$

being actually produced.

The author is engaged with researches which seek to determine whether the action of iodine and mercuric oxide upon carbon compounds is in general an oxidising action.

M. M. P. M.

## Dinitronaphthalene.

By C. Liebermann and W. Hammerschlag (Deut. Chem. Ges. Ber., ix, 333).

The authors have previously shown that in the dinitronaphthol of Martius, the two nitroxyl-groups occupy the $\alpha$- and $\beta$-positions in the same nucleus. They have now succeeded in obtaining the dinitronaphthalene from which the dinitronaphthol is derived.

Acetonaphthalide in acetic solution, when heated on the water-bath with an equal weight of fuming nitric acid till gas begins to be evolved, yields dinitroacetonaphthalide, $C_{10}H_5(NO_2)_2.N.H(C_2H_3O)$, a body crystallising in long needles melting at 247°, and yielding, when heated to 160° with alcoholic ammonia, dinitronaphthylamine, which crystallises in lemon-yellow needles melting at 235°. To obtain dinitronaphthalene, this last product is dissolved in strong sulphuric acid, and water is added till the whole forms a semi-fluid magma, which is treated with nitrous gas and afterwards mixed with alcohol, the reaction which then takes place causing sufficient rise of temperature to decompose the diazo-compound. Water is added, and the mass thereby thrown down, after boiling with potash to decompose any remaining dinitronaphthylamine, is crystallised from alcohol. The product has the composition of dinitronaphthalene. It forms beautiful white or yellowish needles melting at 144°, and therefore differs from the two previously known dinitronaphthalenes which melt at 170° and 214° respectively.

The foregoing reactions are expressed by the equations:—

$$\underset{\text{Dinitroacetonaphthalide.}}{C_{10}H_5(NO_2)_2NH.C_2H_3O} + NH_3 = C_2H_3(NH_4)O_2 + \underset{\text{Dinitronaphthylamine.}}{C_{10}H_5(NO_2)_2NH_2};$$

$$C_{10}H_5(NO_2)_2.NH_2 + NO_2H + H_2 = N_2 + 2H_2O + \underset{\text{Dinitronaphthalene.}}{C_{10}H_6(NO_2)_2}.$$

J. R.

## Action of Phosphorus Pentachloride on β-Naphthol. By P. T. Cleve and H. Juhlin Dannfelt (Bull. Soc. Chim. [2], xxv, 258).

Some β-naphthol prepared from β-napthylsulphurous acid, was treated with phosphorus pentachloride, and the resulting mass heated in a retort traversed by a current of steam. The condensed water soon deposited a solid body, which was purified by boiling with alcoholic potash, and distillation, and was found to be β-monochlornaphthalene. Thus obtained, it is a crystalline mass resembling stearin. It fused at 55·5°, and boiled at 256·5° (corrected).

C. H. P.

## Sulphonaphthalide.

By P. T. Cleve (Bull. Soc. Chim. [2], xxv, 256).

This substance, first obtained by Berzelius, the author obtained in the preparation of naphthylsulphurous acid. It crystallises in long needles, melts at 175·5°, and solidifies to a transparent vitreous mass. It is insoluble in water, difficultly soluble in alcohol and ether, very soluble in benzene, and is not attacked by alkaline solutions. Its formula is determined to be $C_{10}H_7SO_2.C_{10}H_7$, as substantiated by the following facts, though no direct estimation of the sulphur was effected. When a mixture of sulphonaphthalide and phosphorus pentachloride is heated to 180° in a retort, a reaction occurs, phosphorus

trichloride and a solid body being found in the receiver, and a chloride, attackable by ammonia, together with a larger quantity of the solid body, remaining in the retort. After boiling this residue with ammonia, the insoluble mass was treated with ether. The body dissolved by the ether, was mixed with that obtained from the receiver, and after purification with water, the whole was distilled. The distillate solidifies to a stearin-like mass, which melts at 53°, and boils at 254°, and is soluble in alcohol, ether, benzol, and acetic acid. It is a new modification of monochlornaphthalene, $C_{10}H_7Cl$, corresponding with β-naphthol.

The amide crystallised in brilliant needles which melted at 213°; some amide from β-napthylsulphurous acid made for the purpose, melted at 212°, from which it is shown that the sulphonaphthalide, fusible at 175·5°, splits up by the action of phosphorus pentachloride, into β-monochlornapthalene and β-napthylsulphurous chloride, thus

$$C_{10}H_7SO_2.C_{10}H_7 + PCl_5 = PCl_3 + C_{10}H_7Cl + C_{10}H_7SO_2Cl.$$

C. H. P.

## A New Mode of Formation of Aromatic Aldehydes.

By K. Reimer (Deut. Chem. Ges. Ber., ix, 423).

When a mixture of equal numbers of molecules of phenol and chloroform is agitated with excess of soda-ley, a violent reaction takes place, which must at first be moderated by cooling, and ultimately aided by heat. On distilling off the undecomposed chloroform and adding a strong acid, salicylic aldehyde separates in the form of an oil, and may be purified by means of acid sodium sulphite in the usual manner.

The reaction may be represented thus:—

$$C_6H_5ONa + 3NaHO + CHCl_3 = C_7H_5O_2Na + 3NaCl + 2H_2O.$$

Cresol similarly treated yields an aldehyde which is still under investigation.

J. R.

## The Coloured Resorcin Derivatives.

By Rudolf Wagner (Chem. Centr., 1875, 825—827).

This paper contains an account of the discovery of resorcin in resins, &c., by Hlasiwetz; as also of the artificial preparation of it by Körner from iodophenol, and of the other methods, such as the treatment of chlorobenzene-sulphonates with fused sodium hydrate; the action of molten sodium hydrate on phenolsulphonic acid; and by heating benzene-disulphonic acid with sodium hydrate, which last method yields the largest quantity of resorcin.

The properties of resorcin are then described, as well as its behaviour with various reagents, such as the non-formation of a precipitate with lead acetate, which distinguishes it from pyrocatechin, and the non-formation of quinone when resorcin is treated with manganese dioxide

and sulphuric acid, which distinguishes resorcin from its isomeride hydroquinone.

The properties and formation of the azo-compounds discovered by Weselsky are also described. The diazo-compound ($C_{18}H_{12}N_2O_6$) being formed when nitrous acid is passed into an ethereal solution of resorcin, this substance when treated with concentrated hydrochloric acid yields diazo-resorufin, $C_{36}H_{18}N_4O_9$, according to the equation $2C_{18}H_{13}N_2O_6 - 3H_2O = C_{36}H_{18}N_4O_9$. Both diazoresorcin and diazo-resorufin give hydro-diazoresorufin hydrochloride, $C_{36}H_{18}N_4O_9H_{12} + 3HCl$, with tin and hydrochloric acid.

Tetrazoresorcin is produced when diazoresorcin is heated with concentrated nitric acid: diazoresorufin with nitric acid yields tetrazo-resorufin nitrate, in appearance somewhat like potassium permanganate: finally, by treating this last compound with tin and hydrochloric acid, hydroimidotetrazoresorufin hydrochloride is formed.

When resorcin is heated with phthalic anhydride to 195°—200° (Bayer and Fischer), fluorescein is produced—

$$2(C_6H_4(OH)_2) + C_8H_4O_3 = C_{20}H_{12}O_5 + 2H_2O.$$

This substance is a yellow dye, which is changed into red by the action of bromine-water, forming tetrabromfluoresceïn ($C_{20}H_8Br_4O_5$). In all probability natural dyes will be obtained synthetically from resorcin.

E. W. P.

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**On Gentisin.** By H. Hlasiwetz and J. Habermann (Liebig's Annalen, clxxx, 343—349).

A previous paper on this subject appeared in abstract in this Journal (1875, 572). Further research has shown that pyrogentisic acid is identical with hydroquinone. Of the various melting-points of the latter body hitherto given none are correct: the true melting-point is 169° (uncorr.). Gentisic acid has been found to be identical with oxysalicylic acid, which melts when pure at 196°—197°.

Gentisin, when treated with sodium-amalgam, yields a compound having the formula $C_{13}H_{10}O_4$, which differs from that of gentisin ($C_{14}H_{10}O_5$) by CO; and when fused gentisin is treated with dry hydrochloric acid it yields methyl chloride. Hence gentisin contains the radicle methyl. In the former paper a diacetyl-gentisin was described, showing that gentisin contains two hydroxyl-groups. These facts admit of explanation on the assumption that gentisin is formed by the combination of phloroglucin with a body isomeric with piperonal, thus:

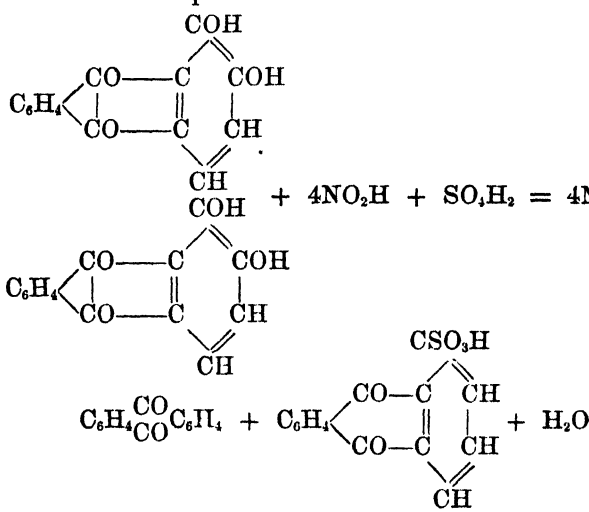
$$C_6H_2\left\{\begin{matrix} CH_3 \\ O \\ O \\ COH \end{matrix}\right. + C_6H_3\left\{\begin{matrix} OH \\ OH \\ OH \end{matrix}\right. - H_2O = \begin{matrix} C_6H_2\left\{\begin{matrix} CH_3 \\ O \\ O \end{matrix}\right. \\ | \\ CO \\ | \\ C_6H_3\left\{\begin{matrix} OH \\ OH \end{matrix}\right. \end{matrix}.$$

Piperonal isomer. Phloroglucin. Gentisin.

J. R.

**Reaction of Alizarin with Nitrous Acid.** By C. NIENHAUS (Deut. Chem. Ges. Ber., viii, 774).

WHEN artificial alizarin is dissolved in concentrated sulphuric acid, and potassium nitrite added into the solution, or when nitrous acid gas is passed in, the original intense red coloration changes into a brown: a drop of the mixture added to caustic soda-solution no longer gives the violet reaction of alizarin, but a yellowish-red. On further addition of the nitrite, the solution finally becomes dark-yellow, and with soda gives no coloration, but a precipitate of anthraquinone. The filtrate contains anthraquinone-monosulphonic acid. The anthraquinone obtained corresponds with one-third of the alizarin employed. The reaction takes place as follows:



In case the artificial alizarin should have contained anthraquinone already formed, natural alizarin was subjected to the same process, but with the same results. The coloration with soda shows the change of alizarin into monoxyanthraquinone. Purpurin treated with nitrous acid also yielded anthraquinone, but the formation of alizarin from purpurin could not be so detected, as the intense red reaction of purpurin changed directly into the wine-red, and not into the violet. This agrees with Rosenstiehl's observation, that purpurin by reduction forms purpuroxanthin, and not alizarin.

E. W. P.

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**Eosin.** By BINDSCHEDLER and BUSCH (Chem. Centr., 1875, 743).

HOFMANN'S researches have shown that eosin is a brominated derivative of fluoresceïn. The greatest difficulty in the manufacture of eosin consists in the preparation of resorcin which is the starting point in the manufacture. The authors find that Egli's method—which consists in forming benzenedisulphonic acid and then hydroxylating the com-

pound—works well in practice. The bromination of fluoresceïn offers no great difficulties: if silk be dyed yellow with this substance, and be then immersed in very dilute bromine-water, the yellow is quickly changed to red owing to the production of eosin.

M. M. P. M.

**On Coniferyl- and Vanillin-compounds.** By FERD. TIEMANN (Deut. Chem. Ges. Ber., ix, 409—423).

A SUMMARY of the various papers bearing on this subject hitherto published by the author and other chemists, of which abstracts have already appeared in this Journal.

J. R.

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**A New Hydroxybenzoic Acid.** By O. EMMERLING and A. OPPENHEIM (Deut. Chem. Ges. Ber., ix, 326—328).

OXYUVITIC acid yields, by oxidation with chromic acid, or with sulphuric acid and potassium permanganate, a new acid which is precipitated from its solutions by hydrochloric and sulphuric acids. It crystallises in thin colourless needles melting at 274·5°, and decomposing at a higher temperature. Analysis of this substance leads to the formula $C_7H_8O_3$, which is that of a hydroxybenzoic acid. The calcium salt crystallises in small, nearly colourless needles, agreeing exactly in composition with the formula $(C_7H_7O_3)_2Ca + 2H_2O$: the water goes off at 160°. The silver-salt, $C_7H_7AgO_3$, is anhydrous and not quite insoluble in water. Neither the acid nor its calcium salt yields phenol when heated. The new acid, when fused with potash, is resolved into water and benzoic acid.

J. R.

**Monobromoparatoluic Acid from Paratoluic Acid and Bromine.** By A. BRÜCKNER (Deut. Chem. Ges. Ber., ix, 407).

THIS acid is easily obtained by adding dry paratoluic acid to a large excess of dry bromine, and after 12 hours allowing the excess of bromine to evaporate in the cold. The product dissolves sparingly in water, freely in alcohol, and crystallises from the solutions in needles which melt at 204°. It sublimes in laminæ. The barium salt, $(C_8H_6BrO_2)_2Ba + 4H_2O$, crystallises in delicate needles. This acid is identical with that obtained by Jannasch and Dickmann by the oxidation of bromoparaxylene.

J. R.

**Oxidation of Isoxylene to Metatoluic Acid.** By A. BRÜCKNER (Deut. Chem. Ges. Ber., ix, 405—407).

PURE isoxylene (obtained by heating commercial xylene from coal-tar with dilute nitric acid for some time, and distilling in a current of steam, the hydrocarbon remaining unattacked), when heated to 130°—150° for a day or two with nitric acid in sealed tubes, yields a mix-

ture of metatoluic and isophthalic acids. These products are separated by distilling the mixture in a current of steam, when the former alone goes over. The metatoluic acid thus obtained crystallises from water in long needles or prismatic crystals melting at 105°—106°.

J. R.

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## β-Naphthoic Acid.

By PAUL VIETH (Liebig's Annalen, clxxx, 305—326).

THE author has prepared this acid on the large scale by the process of Merz and Mühlhäuser, which consists in heating naphthalene with sulphuric acid, neutralising the naphthalene-sulphonic acid thereby formed with soda, distilling the sodium salt with potassium cyanide, and boiling the resulting naphthyl cyanide with alcoholic potash. A mixture of the potassium salts of α- and β-naphthoic acid is thus obtained, the constituents of which are separated by converting them into calcium salts, the α-naphthoate dissolving easily, the β-naphthoate very sparingly in water. The calcium salts are finally decomposed by hydrochloric acid. The successive steps in this process are minutely described in the original paper.

β-Naphthoic acid, after being purified and sublimed, melts at 182°, and gives on analysis numbers agreeing with the formula $C_{11}H_8O_2$.

*Salts of β-Naphthoic Acid.*—The potassium salt, $C_{11}H_7O_2K.\frac{1}{2}H_2O$, obtained by dissolving β-naphthoic acid in potash and evaporating the solution, forms large yellowish laminæ of fatty lustre, easily soluble in water and alcohol. The sodium salt, obtained in a similar manner, forms small tables, dissolving very easily in water and alcohol, and crystallising from the latter in needles. Both salts are hygroscopic. The silver salt, $C_{11}H_7O_2Ag$, is thrown down as a white flocculent precipitate on adding the sodium salt to silver nitrate. It is slightly soluble in hot water, insoluble in cold water and alcohol. It turns violet in the light, like silver chloride. The magnesium salt, $(C_{11}H_7O_2)_2Mg.5H_2O$, obtained by boiling magnesium carbonate with β-naphthoic acid and water, forms a white pulverulent and efflorescent mass, soluble in water and alcohol.

*β-Naphthoic chloride*, $C_7H_7OCl$, was obtained by distilling a mixture of β-naphthoic acid and phosphorus pentachloride. It is a white crystalline body, melting at 43° to a clear faintly-yellow liquid, which boils at 304°—306° without decomposition. It is soluble in ether, chloroform, and benzene, and dissolves also in alcohol, with which, however, it forms hydrochloric acid and ethyl β-naphthoate. In presence of water it is resolved into hydrochloric and β-naphthoic acids.

*Methyl β-naphthoate* is formed, together with hydrochloric acid, when β-naphthoic chloride is dissolved in methyl alcohol: it crystallises out on evaporating the liquid. It forms white shining laminæ, easily soluble in methyl and ethyl alcohols, ether, chloroform, and benzene. The crystals melt at 77° to a clear liquid, which boils about 290°. The ether has an agreeable fruity odour. Its composition agrees with the formula $C_{10}H_7CO.OCH_3$.

*Ethyl β-naphthoate*, $C_{10}H_7CO.OC_2H_5$, prepared like the methyl-ether, forms a colourless oily liquid, of faint odour, soluble in alcohol, ether,

chloroform, and benzene. It crystallises from the alcoholic solution in the cold in small laminæ, which melt with the warmth of the hand. Boiling point, 308°—309°.

*β-naphthoic amide*, $C_{10}H_7CO.NH_2$. This substance was obtained by heating over the water-bath a mixture of equal parts of β-naphthoic chloride and ammonium carbonate, and exhausting the dry crumbly mass thereby formed with alcohol, which deposited crystals of the amide on evaporation. After being purified by dissolving it in alcohol and precipitating the solution with water, it crystallises from alcohol in colourless tables which dissolve in alcohol, ether, chloroform, and benzene, melt at 192°, and volatilise without decomposition at a higher temperature.

*β-Naphthoic carbamide.* Urea reacts in the same manner as ammonium carbonate with β-naphthoic chloride. The alcoholic extract leaves on evaporation a white crystalline powder of β-naphthoic carbamide, which dissolves sparingly in alcohol and chloroform, and very slightly in ether and benzene. The crystals melt at 215°, and do not volatilise undecomposed. The numbers furnished by analysis agree with the formula—

$$\begin{array}{l} NH_2 \\ | \\ CO \\ | \\ NH.C_{10}H_7.CO. \end{array}$$

*β-Naphthoic anilide* is formed when a solution of β-naphthoic chloride in benzene is mixed with an equal weight of aniline also dissolved in benzene; or when β-naphthoic acid is heated to 120° with excess of aniline. It crystallises in small shining laminæ soluble in alcohol and ether, and in warm chloroform and benzene. The crystals melt at 170° and sublime in large laminæ at a higher temperature. Analyses agree with the formula $C_{10}H_7.CO.NH.C_6H_5$.

*β-Naphthoic toluidide*, $C_{10}H_7\,CO.NH.C_7H_7$. Obtained in the same manner as the foregoing substance by the action of toluidine on β-naphthoic chloride, both dissolved in benzene. It forms silky colourless needles easily soluble in alcohol and chloroform, sparingly in ether and benzene, and melting at 191°.

*β-Naphthoic naphthylamide*, $C_{10}H_7.CO.NH.C_{10}H_7$, is obtained in the same way as the two foregoing bodies. It crystallises in small needles, which form violet solutions with alcohol, ether, chloroform, and benzene. It melts at 157° and solidifies in a glassy mass on cooling.

α-Naphthoic and β-naphthoic acids both yield phthalic acid by oxidation with chromic and acetic acids.

J. R.

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## Camphic Acid.

By J. DE MONGOLFIER (Bull. Soc. Chim. [2], xxv, 13—17).

THIS acid, which Berthelot obtained by treating camphor with alcoholic potash, is also formed by the action of oxygen on sodium camphor.

$$C_{10}H_{15}NaO + O = C_{10}H_{15}NaO_2.$$

Thus on heating a solution of the sodium-compound in benzene to 100° in a tube filled with oxygen, the gas was completely absorbed in a few hours, while at the common temperature it took two days. To prepare camphic acid, the product of the action of sodium on camphor is dissolved in coal-tar naphtha boiling at 125°, and a current of air is passed to the gently-boiling liquid. After the reaction is finished, the naphtha is distilled off, the residue exhausted with water, and the solution fractionally precipitated with an acid. First a resin is precipitated carrying down camphoric acid, which is also formed, and then camphic acid is thrown out, while some camphoric acid remains in solution.

Camphic acid yields, by double decomposition, the salt $(C_{10}H_{15}O_2)_2Cu$ as a green powder, which is partly soluble in ether, benzene, chloroform, and strong alcohol. The green alcoholic solution deposits a viscid almost black mass, drying up to a dark-green brittle substance consisting of $C_{10}H_{16}O_2 + (C_{10}H_{15}O_2)_2Cu$.

By oxidising camphic acid with potassium permanganate, it is converted into oxycamphic acid, $C_{10}H_{16}O_3$, which does not crystallise, and resembles camphic acid, but is more liquid. At the same time some acetic acid and camphoric acid are formed, as well as an acid which appears to be toluic acid.

C. S.

## The Tannic Acid of the Oak. By J. Oser (Chem. Centr., 1875, 517).

Reference is made to the fact that the green leaves of the oak contain a considerable quantity of quercitannic acid, so that they would prove a good material for tanning purposes. The leaves of the oak are also found to contain ellagic acid. The green gall-nuts contain principally tannic and ellagic acid, besides trifling quantities of quercitannic acid. Attention is directed to two sources of error in the determination of the astringent principles of oak-bark by Löwenthal's method. Firstly, that the oxygen absorbed by equal quantities of quercitannic acid and tannin is not the same, although always assumed to be so, but is in the proportion of 1 : 1·5; and, secondly, that the watery extracts contain, besides tannin, considerable quantities of other substances which become oxidised by the potassic permanganate.

H. H. B. S.

## Anthraflavic and Iso-anthraflavic Acids. By E. Schunck and H. Roemer (Deut. Chem. Ges. Ber., ix, 379—383).

In a previous paper, the authors described a new acid isomeric with anthraflavic acid. To this acid, which has now been more fully investigated, they give the name *iso-anthraflavic acid*. It was obtained by treating crude alizarin (prepared chiefly from dianthraquinone-sulphonic acid) with lime-water, and precipitating the red solution with hydrochloric acid. When pure, it crystallises in long yellow needles, the composition of which agrees with the formula $C_{14}H_8O_4.H_2O$. The

barium salt, $C_{14}H_6BaO_4$ + aq., is very easily soluble in water, and crystallises with difficulty in dark-red shining needles.

*Properties of the Isomeric Acids.*

| *Iso-anthraflavic Acid.* | *Anthraflavic Acid.* |
|---|---|
| Crystallises with water from weak spirit. | Crystallises without water. |
| Dissolves with deep-red colour in strong hot sulphuric acid. | Dissolves with yellow colour in strong sulphuric acid. |
| Easily soluble in cold baryta-water. | Insoluble in cold baryta-water. |
| Easily soluble in lime-water. | Sparingly soluble in cold, nearly insoluble in hot lime-water. |
| Solutions in alkalis and alkaline earths are deep-red. | Solutions in alkalis and alkaline earths are more or less yellow. |

Both acids melt above 330°, and are more freely soluble in alcohol than in glacial acetic acid, and nearly insoluble in benzene, chloroform, and ether. From aqueous solutions of the barium salts, carbon dioxide throws down the free acids, but the salts are re-formed on boiling. Both acids are soluble in alcoholic lead acetate. Both sublime in yellow needles and laminæ.

*Tetrabromo-iso-anthraflavic Acid*, $C_{14}H_4Br_4O_4$.—Obtained by dropping a large excess of bromine into an alcoholic solution of the acid. Yellow needles, sparingly soluble in alcohol and more freely in glacial acetic acid.

*Tetrabromo-anthraflavic Acid.*—Prepared like the preceding compound. Nearly insoluble in all ordinary solvents.

*Diacetyl-iso-anthraflavic Acid*, $C_{14}H_6(C_2H_3O)_2O_4$.—Formed by the action of acetic anhydride on anthraflavic acid at 160°—180°. Dissolves sparingly in alcohol and glacial acetic acid, and separates from the latter in pale-yellow microscopic crystals, which melt at about 195°.

*Diacetyl-anthraflavic Acid.*—Previously obtained by Perkin. Crystallises more easily than the foregoing compound. Melts at 227°.

*Diethyl-iso-anthraflavic Acid*, $C_{14}H_6(C_2H_5)_2O_4$.—Produced by heating iso-anthraflavic acid to 120° with soda-ley, ethyl iodide, and alcohol. It crystallises from alcohol in long shining pale-yellow needles, which are insoluble in water, sparingly soluble in alcohol and ether, and more freely in glacial acetic acid and benzene. Strong sulphuric acid colours it red-violet. The solution exhibits two indistinct absorption-bands in the green and yellow. Melts at 193°—194°.

*Diethyl-anthraflavic Acid.*—Prepared like the foregoing, which it resembles in most respects: the crystals, however, are somewhat paler, and the solution in sulphuric acid is red, and shows a distinct absorption-band between the green and blue. Melts at 232°, and solidifies on cooling in large prismatic crystals.

*Dimethyl-anthraflavic Acid.*—Prepared in a similar manner to the two preceding compounds, which it resembles in general. Melts at 247°—248°.

J. R.

**Chrysammic Acid and Chrysazin.** By C. LIEBERMANN and F. GIESEL (Deut. Chem. Ges. Ber., ix, 329—332).

IN a former paper it was shown that chrysammic acid is derived from chrysazin, and that probably the direct product of the action of nitric acid on chrysazin, but not on chrysophanic acid, is chrysammic acid. A comparative examination of the three acids has fully confirmed this view.

*Chrysammic Acid from Aloes.*—This acid, when allowed to crystallise slowly from its solution in hot fuming nitric acid, forms small compact measureable crystals, with brilliant faces. Previously it had been obtained only in small gold-yellow scales.

*Tetranitrochrysazin*, $C_{14}H_4(NO_2)_4O_4$, crystallises in exactly the same form as chrysammic acid, the crystals being short clinorhombic prisms.

*Tetranitrochrysophanic Acid*, $C_{15}H_6(NO_2)_4O_4$, crystallises from nitric or acetic acid in small gold-yellow laminæ, never in compact crystals.

The salts of chrysammic acid, many of which were examined, are also identical with those of nitrochrysazin, but more or less different from those of nitrochrysophanic acid. The latter are more soluble, seldom crystallisable, and generally not quite pure. The salts were obtained by boiling the respective acids with acetates, and crystallising the resulting precipitates.

The *potassium salt* of nitrochrysazin, $C_{14}H_2(NO_2)_4O_4K_2$, forms sparingly soluble anhydrous needles, having a metallic lustre. Potassium nitrochrysophanate, $C_{15}H_4(NO_2)_4O_4K_2$, crystallises in thin red needles, soluble with difficulty in saline liquids but easily in water.

The *calcium salt* of nitrochrysazin, $C_{14}H_2(NO_2)_4O_4Ca$, forms gold-yellow lustrous needles. Calcium nitrochrysophanate, $C_{15}H_4(NO_2)_4O_4Ca$, crystallises in thread-like, indistinct needles devoid of lustre.

The *magnesium salt* of nitrochrysazin forms fine reddish-yellow lustrous crystals, which turn brown on drying and recover their original colour when moistened. Magnesium nitrochrysophanate is a red sparingly soluble powder.

Oxychrysazin, the authors find, is not identical with either of its isomerides purpurin and isopurpurin, and therefore forms the third known oxyanthraquinone.

*Triacetylpurpurin*, $C_{14}H_5(C_2H_3O)_3O_5$, obtained by heating purpurin to 170° with acetic anhydride, forms yellowish needles melting at 190°—193°.

*Triacetyloxychrysazin* forms pale-yellow needles melting at 192°—193°.

*Triacetylisopurpurin* melts, according to Perkin, at 220°—222°.

Purpurin and oxychrysazin are readily distinguished by the colours of their alkaline solutions (purpurin, red; oxychrysazin, blue), and by the well-known optical characters of purpurin, which do not pertain to oxychrysazin.

J. R.

**Substituted Ureas.** By W. MICHLER (Deut. Chem. Ges. Ber., ix, 396—400).

WHEN carbon oxychloride is passed into a solution of diphenylamine in chloroform, the gas is absorbed and diphenylamine hydrochloride is deposited. The chloroform leaves, on evaporation, a body crystallising from alcohol in fine white laminæ, and giving, on analysis, numbers agreeing with the formula $Cl—CO—N(C_6H_5)_2$. This substance, *carbonyl-diphenylamidochloride* (*Diphenylharnstoff-chlorid*) is decomposed by alcoholic potash, when heated therewith, in the manner shown by the equation—

$$Cl—CO—N(C_6H_5)_2 + H_2O = HCl + CO_2 + NH(C_6H_5)_2.$$

*Unsymmetrical Diphenylurea.*—Carbonyl-diphenylamidochloride reacts with alcoholic ammonia in the following manner:—

$$Cl—CO—N(C_6H_5)_2 + NH_3 = HCl + NH_2—CO—N(C_6H_5)_2.$$

The product, which is isomeric with carbanilide, crystallises in long needles melting at 189°. Like the derivatives of diphenylamine generally, it forms a fine blue solution with hot sulphuric acid. By distillation with solid potash it is resolved into diphenylamine, carbon dioxide, and ammonia.

Diphenylurea is similarly decomposed by ammonia when heated therewith to 150° for some hours, diphenylamine being formed.

*Triphenylurea.*—When carbonyl diphenylamidochloride, dissolved in chloroform, is heated to 130° with 2 mol. of aniline, a reaction takes place, resulting in the formation of triphenylurea—

$$\begin{matrix} C_6H_5 \\ H \end{matrix}\!\!>\!N—CO—N<\!\!\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}.$$

This body is resolved by distillation with solid potash into aniline, carbon dioxide, and diphenylamine—

$$\begin{matrix} C_6H_5 \\ H \end{matrix}\!\!>\!N—CO—N<\!\!\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} + H_2O = CO_2 + NH(C_6H_5)_2 + NH_2C_6H_5.$$

Triphenylurea heated to 150° with excess of aniline, reacts in the following manner:—

$$\begin{matrix} C_6H_5 \\ H \end{matrix}\!\!>\!N—CO—N<\!\!\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} + NH_2C_6H_5 = CO<\!\!\begin{matrix} NHC_6H_5 \\ NHC_6H_5 \end{matrix} + NH(C_6H_5)_2.$$

Carbanilide.

*Carbonyl-phenylethylamidochloride.* — Carbon oxychloride, passed into ethylaniline diluted with chloroform, reacts with it to form a body crystallising in small white needles, which have an agreeable

odour, melt at about 52°, and agree in composition with the formula

$$Cl—CO—N\begin{cases}C_2H_5\\C_6H_5\end{cases}.$$

Other analogous derivatives of urea are under investigation. The foregoing results show that the behaviour of carbon oxychloride with secondary aromatic amines is different from its behaviour with fatty amines; for whilst diethylamine is converted directly into tetrethylurea, aromatic amines yield only bodies of the general formula

$$CO\begin{cases}Cl\\NRR_1\end{cases}.$$

J. R.

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**Sulpho-phenyl-urea.** By PH. DE CLERMONT (Compt. rend., lxxxii, 512).

THIS substance may easily be prepared by acting at 100° with hydrochloride of phenylamine on ammonium sulphocyanate, when the following reaction occurs:—

$$C_6H_7N.\,HCl + CN.\,NH_4S = CS,\,NH_2.\,NH.\,C_6H_5 + NH_4Cl.$$

After evaporating to dryness, and heating for some hours, the residue is washed with water and dissolved in boiling alcohol, which, on cooling, deposits the sulphophenylurea in crystals. These are very little soluble in cold, and slightly so in boiling water or cold alcohol, but dissolve abundantly in boiling alcohol. Cold hydrochloric acid dissolves sulphophenylurea without change; but it is decomposed when heated with the acid to 120° in sealed tubes, thus:—

$$CS,\,NH_2.\,NH.\,C_6H_5 + 2HCl + 2H_2O = CO_2 + H_2S + NH_4Cl + C_6H_7N.\,HCl.$$

Heated with ammonia in a close vessel to 140°, the phenylamine is displaced by the ammonia, and ammonium sulphocyanate is found among the products of the reaction. Heated alone in a sealed tube to 180°, its decomposition gives rise to a number of complex substances, amongst which sulphocyanic acid, ammonia, phenylamine, ammonium sulphide, and diphenylsulphocarbamide may be recognised.

R. R.

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**Diazobromobenzene and Nitro-ethane.** By H. WALD (Deut. Chem. Ges. Ber., ix, 393—394).

THE diazo-derivative of amidobenzoic acid reacts with nitroethane-potassium, to form the compound

$$C_6H_4\begin{cases}COOH\\N_2—C_2H_4NO_2\end{cases},$$

which, however, it was not found possible to separate from the diazo-amidobenzoic acid formed at the same time.

The diazo-salt obtained by adding potassium nitrite to a solution of parabromaniline in nitric acid, gives, with nitroethane-potassium, a bulky precipitate consisting of the potassium-salt of the compound $C_6H_4Br—N_2—C_2H_4NO_2$. This body crystallises from alcohol in brick-red shining crystals soluble in ether, chloroform, &c. It melts with decomposition at 135°—138°. A solution of the potassium-salt gives coloured precipitates with silver, lead, and copper salts.

J. R.

**Nitro-ethane and Diazonitrobenzene.** By F. HALLMANN (Deut. Chem. Ges. Ber., ix, 389—392).

WHEN a solution of nitraniline is added to a dilute solution of potassium nitrite, a pale-yellow precipitate is thrown down, which forms, when dry, a light, highly-electric powder. This substance is almost insoluble in ordinary solvents, and indifferent towards acids and alkalis. It melts at 175°—176°, and gives on analysis numbers agreeing with the formula $C_{12}H_9N_5O_4$. Its constitution is not yet determined.

The solution of diazonitrobenzene nitrate filtered from the foregoing compound, gives, on addition of nitroethane-potassium, a precipitate of an acid having the formula—

$$C_6H_4NO_2—N_2—C_2H_4NO_2.$$

This body forms, when pure, a yellow powder soluble with red colour in alkalis, and easily soluble in hot alcohol. The sodium salt is sparingly soluble in water: its solution gives coloured precipitates with silver, copper, and lead salts. When treated with tin and hydrochloric acid, the acid yields a body which forms with tin tetrachloride a crystalline compound agreeing in composition with the formula $C_8N_{16}N_4Cl_2 + SnCl_4$.

J. R.

**Mixed Azo-compounds.** By VICTOR MEYER (Deut. Chem. Ges. Ber., ix, 384—386).

PRIMARY nitropropane reacts with diazobenzene nitrate to form nitropropylazobenzene,

$$CH_3—CH_2—C\begin{cases} H \\ NO_2 \\ N_2—C_6H_5 \end{cases},$$

a body crystallising in dark-orange needles easily soluble in hot alcohol. The crystals melt at 98°—99°, and dissolve in alkalis, forming deep red solutions. Like the homologous ethane and methane derivatives, which it otherwise resembles, it is an acid body, and is thereby distinguished from the isomeric isopropyl-compound, which is a neutral substance.

J. R.

## Mixed Azo-compounds. By J. BARBIERI (Deut. Chem. Ges. Ber., ix, 386—389).

*Nitroethyl-azoparatolyl*, $C_6H_4\begin{cases}CH_3\\N_2—C_2H_4.NO_2\end{cases}$.—This body is obtained by the reaction of diazoparatolyl nitrate on nitroethane. It forms fine orange-red prisms, having a peculiar steely lustre, and melting at 133°. In other respects, it closely resembles the isomeric nitropropyl-azophenyl. It dissolves in alkalis, forming deep-red salts. An aqueous solution of the sodium salt gives coloured precipitates (yellow to red) with mercury, silver, lead, copper, and zinc salts.

*Nitroethyl-azo-orthotolyl.*—Obtained like the foregoing substance, which it resembles in properties. It crystallises in orange needles, which melt at 87°—88°.

J. R.

## Action of Hydrogen Sulphide on Alkaloïds. By E. SCHMIDT (Liebig's Annalen, clxxx, 287—304).

ALMOST all the known vegetable bases are acted upon by hydrogen sulphide. The substances thereby formed, though in some cases definite compounds, appear for the most part to be mixtures which cannot be separated, owing to the facility with which they are decomposed. The author has examined more particularly the compounds formed with strychnine and brucine.

*Strychnine.*—When an alcoholic solution of strychnine is saturated with hydrogen sulphide and left at rest for some time, it gradually deposits fine orange-red needles of a substance to which Schmidt attributes the formula $2C_{21}H_{22}N_2O_2,3H_2S_2$. This substance differs in colour and crystalline form from that which Hofmann obtained by the action of ammonium sulphide on strychnine, but cannot be distinguished therefrom by analysis. When kept for a day or two, it gives off hydrogen sulphide and slowly changes colour, whereas Hofmann's compound keeps for months without alteration. It was ascertained by direct experiment that this compound is formed only in presence of oxygen, not when the air is completely excluded. Its formation may be represented by the equation—

$$2C_{21}H_{22}N_2O_2 + 6H_2S + 3O = \begin{matrix}C_{21}H_{22}N_2O_2\\C_{21}H_{22}N_2O_2\end{matrix}\left\{\begin{matrix}H_2S_2\\H_2S_2\\H_2S_2\end{matrix}\right. + 3H_3O.$$

The compound is decomposed by mineral acids, with separation of oily drops of hydrogen bisulphide and formation of strychnine salts.

*Brucine.*—When hydrogen sulphide is passed into a strong solution of brucine in alcohol, freely exposed to the air, the liquid immediately assumes a yellow colour, and after a time deposits yellow needles, which, on prolonged standing, become covered with a yellowish-red layer of another sulphur-compound. The yellow needles gave, on analysis, numbers agreeing with the formula $C_{23}H_{26}N_2O_4H_2S_2 + 2H_2O$, which is that of a compound of 1 mol. of brucine with 1 mol. of

hydrogen bisulphide. This formula, however, is of no value, for the substance after drying possesses altered properties, and its composition is not represented by the formula $C_{23}H_{26}N_2O_4H_2S_2$. The crystals are prismatic, insoluble in the ordinary solvents, and undergo partial decomposition when kept. They are decomposed by mineral acids, with separation of hydrogen bisulphide and formation of brucine salts. The melting point is about 125°.

A second derivative of brucine is easily obtained by passing hydrogen sulphide into a dilute alcoholic solution of the alkaloïd (1 in 100), till the liquid assumes a deep-yellow colour and allowing it to stand in loosely-covered vessels. In the course of 24 hours there is formed a deposit of ruby-red crystals, which, after washing with alcohol and ether, have the composition represented by the formula $C_{23}H_{26}N_2O_4\begin{matrix}H_2S_2\\H_2S_2\end{matrix}$. The crystals belong to the triclinic system. In their behaviour they closely resemble the foregoing yellow compound.

The formation of these brucine-compounds is dependent, like that of the strychnine-compound, on the presence of oxygen, for if the air be perfectly excluded not a trace of them is produced. The following equations may, perhaps, represent their formation:—

$$C_{23}H_{26}N_2O_4 + 2H_2S + O = H_2O + C_{23}H_{26}N_2O_4H_2S_2;$$

$$C_{23}H_{26}N_2O_4 + 4H_2S + O_2 = 2H_2O + C_{23}H_{26}N_2O_4\left\{\begin{matrix}H_2S_2\\H_2S_2\end{matrix}\right..$$

J. R.

## Amidines of Monobasic Organic Acids. By A. Bernthsen (Deut. Chem. Ges. Ber., ix, 429—435).

The action of ammonia on phenyl thiacetamide in presence of air results in the formation of a new base, *phenylacetamimide*, $C_6H_5—CH_2—C\begin{matrix}\diagup NH\\\diagdown NH_2\end{matrix}$, as previously described by the author. The base is formed also by the action of desulphurising agents on ammonia and the thiamide: with mercuric chloride the reaction is as follows:—

$$C_6H_5—CH_2—CSNH_2 + 2NH_3 + HgCl_2 = HgS + NH_3.HCl + C_6H_5—CH_2—C\begin{matrix}\diagup NH\\\diagdown NH_2\end{matrix}HCl.$$

The base absorbs carbonic dioxide from the air. Its melting point is 83°—89°. It is decomposed by alcohol or water, phenylacetamide and ammonia being formed.

$$C_6H_5—CH_2—C\begin{matrix}\diagup NH\\\diagdown NH_2\end{matrix} + H_2O = C_6H_5—CH_2—C\begin{matrix}\diagup O\\\diagdown NH_2\end{matrix} + NH_3.$$

Several *salts* of the base have been analysed. The acid sulphate crystallises in large tables, easily soluble in alcohol and water. The

neutral oxalate forms white prisms or needles, also soluble in alcohol and water. The acid oxalate, which is less soluble, crystallises in matted needles. The nitrate is crystallisable.

When phenylthiacetamide is heated with aniline hydrochloride, hydrogen sulphide is evolved, and a new base, *phenylacetomonophenylamimide*, $C_6H_5—CH_2—C\begin{cases}NC_6H_5\\NH_2\end{cases}$, is formed—

$$C_6H_5—CH_2—CSNH_2 + C_6H_5—NH_2HCl = H_2S + C_6H_5—CH_2—C\begin{cases}NC_6H_5\\NH_2\end{cases}, HCl.$$

The same base is formed by the reaction of benzyl cyanide and aniline hydrochloride—

$$C_7H_7—CN + C_6H_5—NH_2.\ HCl = C_7H_7—C\begin{cases}NC_6H_5\\NH_2\end{cases}.\ HCl;$$

also by the action of iodine on a mixture of aniline and phenylthiacetamide in alcoholic solution:

$$C_6H_5—CH_2—CSNH_2 + NH_2—C_6H_5 + I_2 = S + HI + C_6H_5—CH_2—C\begin{cases}NC_6H_5\\NH_2\end{cases}.\ HI.$$

Phenylacetomonophenylamimide forms small white needles or laminæ, melting at about 128°, and subliming in long needles. It dissolves sparingly in water and very freely in alcohol and ether. It is a mon-acid base, forming salts which, with the exception of the oxalate, are not crystallisable.

*Phenylacetomonotolylamimide*, $C_6H_5—CH_2—C\begin{cases}NC_7H_7\\NH_2\end{cases}$, a base corresponding to the foregoing, is obtained by similar reactions, toluidine hydrochloride being employed instead of the aniline salt. It crystallises in thick prisms, which dissolve in water, alcohol, and ether, melt at 118°—119°, and sublime at a higher temperature. Its salts are more easily crystallisable than those of the phenyl base.

The action of aniline hydrochloride on thiobenzamide or benzonitril results in the formation of two bases:—

1. *Benzenylmonophenylamimide*, $C_6H_5—C\begin{cases}NC_6H_5\\NH_2\end{cases}$, a white substance dissolving easily in water, and forming salts which are mostly uncrystallisable.

2. *Benzenyldiphenylamimide*, $C_6H_5—C\begin{cases}NC_6H_5\\NHC_6H_5\end{cases}$, nearly insoluble in

water, and identical with Gerhard's product obtained by the action of phosphorus pentachloride on benzanilide. This substance is produced by the action of aniline on the preceding, thus:—

$$C_6H_5—C\begin{matrix}\diagup NC_6H_5\\ \diagdown NH_2\end{matrix} + NH_2—C_6H_5 = C_6H_5—C\begin{matrix}\diagup NC_6H_5\\ \diagdown NHC_6H_5\end{matrix} + NH_3.$$

*Benzenylmonotolylamimide*, $C_6H_5—C\begin{matrix}\diagup NC_7H_7\\ \diagdown NH_2\end{matrix}$, formed by the action of benzonitril on toluidine hydrochloride, crystallises in transparent tables melting at 99°—99·5°. The oxalate and nitrate crystallise in needles.

*Benzenylditolylamimide*, $C_6H_5—C\begin{matrix}\diagup NC_7H_7\\ \diagdown NHC_7H_7\end{matrix}$, is formed together with the preceding base. It crystallises in thick yellowish prisms, less freely soluble than the monotolyl base. It melts at 131°—132°, and sublimes at a higher temperature.

J. R.

**Action of Phosphorus Pentachloride on the Amides of Sulpho-acids.** By O. WALLACH and TH. HUTH (Deut. Chem. Ges. Ber., ix, 424—429).

A PREVIOUS paper on this subject has appeared in abstract in this Journal (1875, 1026).

The substance formed by the action of phosphorus pentachloride on benzenesulphanilide has the composition represented by the formula $C_{12}H_{10}SO_2NCl$. When decomposed with hydrochloric acid, it yields a solution from which alkalis separate solid monochloraniline melting at 70°. The formation and decomposition of the substance must therefore be represented as follows:—

$$C_6H_5SO_2NHC_6H_5 + PCl_5 = PCl_3 + HCl + \underset{\text{Benzene-sulphochloranilide.}}{C_6H_5SO_2NHC_6H_4Cl}:$$

$$C_6H_5SO_2NHC_6H_4Cl + H_2O + HCl = C_6H_5SO_3H + NH_2C_6H_4Cl + HCl.$$

The correctness of this view has been established by direct comparison of synthetically prepared benzene sulphochloranilide (obtained by the reaction of monochloraniline and benzene sulphochloride) with the foregoing product, with which it is identical in properties.

Hence it appears that the action of phosphorus pentachloride on benzene sulphamide is not analogous to its action on benzene sulphanilide. The action in the two cases may indeed be supposed to be represented thus—

$$R.SO_2NHH + PCl_3, Cl_2 = R.SO_2NHCl + PCl_3 + HCl$$
$$R.SO_2NHC_6H_5 + PCl_3, Cl_2 = R.SO_2NHC_6H_4Cl + PCl_3 + HCl$$

but in the former case the product thus formed is further acted on by phosphorus trichloride—

$$RSO_2NHCl + PCl_3 = R.SO_2NCl.PCl_2 + HCl;$$

while in the latter case this action does not take place, as was found by direct experiment.

Benzene sulphotoluide is not acted on by phosphorus pentachloride in the same manner as benzene sulphanilide. It was found impossible to isolate from the product of the action any substance containing chlorine or phosphorus.

J. R.

**Secondary Monamines formed by the Action of Liquid Toluidine on Aniline Hydrochloride.** By CH. GIRARD and ED. WILLM (Bull. Soc. Chim. [2], xxv, 248—252).

WITH the object of preparing liquid phenyltoluidine (phenylpara-cresylamine) aniline hydrochloride was heated with liquid toluidine. The reaction takes place, but the mixture behaves as though it contained free aniline and toluidine and their hydrochlorides. Further complication arises from the fact that the liquid toluidine contains some solid, or orthotoluidine,* which, taking part in the reaction, gives rise to isomeric secondary amines, in which the nitrogen is joined to one phenyl-group and one cresyl-group in the ortho position; or to two cresyl groups, one ortho and one para, or both ortho. The mixture resulting from the reaction contains the six following bases:—

$$\left.\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right\}NH \quad . \quad \left.\begin{matrix}o\text{-}C_6H_4.CH_3\\C_6H_5\end{matrix}\right\}NH \quad . \quad \left.\begin{matrix}p\text{-}C_6H_4.CH_3\\p\text{-}C_6H_4.CH_3\end{matrix}\right\}NH$$

$$\left.\begin{matrix}o\text{-}C_6H_4.CH_3\\o\text{-}C_6H_4.CH_3\end{matrix}\right\}NH \quad . \quad \left.\begin{matrix}C_6H_5\\o\text{-}C_6H_4.CH_3\end{matrix}\right\}NH \quad . \quad \left.\begin{matrix}o\text{-}C_6H_4.CH_3\\p\text{-}C_6H_4.CH_3\end{matrix}\right\}NH.$$

The crude product was washed with hydrochloric acid, and then treated with warm water, which liberated the mixed amines as a blackish liquid, acquiring the consistence of tar on cooling. After due washing, this mass was distilled in a vacuum, a somewhat difficult operation, in consequence of the great frothing which occurs.

Three portions were fractionated, the first passing at 185° under a pressure of 2·5 cm., the second at 240°—242°, the pressure being 15 cm., the third at 260°, the pressure being 17 cm. A portion not examined passed at 300°.

The third portion was semi-fluid, and filled with crystals, which were separated from the liquid portion by filtration, by exposure to cold, and finally by treatment with cold alcohol, which scarcely affects them, whereas it dissolves the fluid portion with facility. The crystals consist of phenylorthocresylamine; they melt at 87°—88°, and distil

* Solid toluidine is usually regarded as the *para* and liquid toluidine (Rosenstiehl's pseudotoluidine) as the *ortho*-modification.—[ED.]

at 307°—308°. The alcoholic mother-liquors deposit other crystals, fusible at 82°, which were found to be solid dicresylamime, the twice ortho body, which distils at 323°.

The original liquid portion, together with the mother-liquors from both of the above bodies (after being freed from alcohol), were dissolved in benzene and treated with gaseous hydrochloric acid; the precipitated hydrochloride filtered, washed with benzol, decomposed with water, distilled, and purified by crystallisation, was found to be diphenylamine.

From the benzene solution remaining after the separation of the diphenylamine, a crystalline substance, fusible at 41° and distilling at 297°—299°, was obtained. Its exact nature is as yet undetermined, but it is considered to be probably phenylparacresylamine.

The alcoholic mother-liquids, deprived as far as possible of the above base, fusible at 41°, afford a liquid base not solidifiable by the cold produced by a mixture of solid carbonic anhydride with ether.

The foregoing bases were converted into the corresponding formamides, to be described in a subsequent paper.

*Action of Phosgene on Diphenylamine.*—53 grams of liquefied phosgene were made to react upon 360 grams of diphenylamine dissolved in benzene, with the object of producing tetraphenylurea; an intermediate body already mentioned by W. Michler, of the formula $CO\left\{\begin{matrix}Cl\\N(C_6H_5)_2\end{matrix}\right.$, was obtained, melting at 85°, crystallisable in alcohol. The benzene solution was filtered, the benzene removed by distillation, and the residue treated with boiling alcohol, which deposits the chloridised body almost wholly on cooling. After removing the alcohol and the remainder of the benzene by distillation, an evolution of hydrochloric acid occurred; the residue yielded to boiling alcohol, a substance which crystallised in hard crystals, which were free from chlorine, and melted at 178°—180°. This substance evidently was tetraphenylurea, formed by the action of excess of diphenylamine on the intermediate body.

C. H. P.

## Action of Oxalic Acid on Diphenylamine.

By C. Girard and E. Willm (Bull. Soc. Chim. [2], xxiv, 99—100).

In the course of a research on the constitution of the blue colouring matter formed by the action of oxalic acid on diphenylamine, the authors discovered amongst the secondary products which accompany the production of the blue, a crystalline compound distilling at 210°—220°, and having the formula of formodiphenylamine $(C_6H_5)_2N.COH$. It is also formed, with elimination of water, by the direct action of formic acid on diphenylamine. It is insoluble in water, but soluble in benzene and in alcohol, crystallising from the latter, by spontaneous evaporation, in voluminous orthorhombic crystals. Treated with sulphuric acid it evolves pure carbonic oxide; the action of both reducing and oxidising agents reproduces diphenylamine. A solution of potassium hydrate, or water alone at 140°, causes it to split up into formic acid and diphenylamine.

With regard to the blue itself, which is obtained in the state of hydrochloride, it appears to contain a complex amine, formed from several diphenylamine residues united by a carbon atom or by the group CH or $CH_2$. Heated in a current of hydrochloric acid, it gives off a gas which burns with a green flame, in all probability methyl chloride. This blue usually occurs in commerce as the double salt of a sulpho-conjugated acid, but the identity of the colouring matters obtained by the action of sulphuric acid on the insoluble blue, and those formed from the sulpho-conjugated acids of diphenylamine by the action of oxalic acid, have not as yet been established.

C. E. G.

**Observations on the Metamorphoses of the Methyl-rosanilines.** By CH. GIRARD and ED. WILLM (Bull. Soc. Chim. [2], xxv, 200).

IT was found that the oxidation of a mixture of methylaniline and dimethylaniline by means of cupric chloride, trimethyl-rosaniline was obtained. A similar product results from the mere action of rosaniline upon trimethyl-rosaniline dimethylate, at the ordinary temperature in alcoholic solution, from which reaction the extreme mobility of the exterior methyl-groups becomes evident, not even a trace of the monomethylate being found in the solution.

C. H. P.

**Action of Ammonia on Rosaniline.** By E. JACQUEMIN (Compt. rend., lxxxii, 261).

PERSOZ and others have shown that rosaniline is capable of uniting directly with ammonia, to form a colourless compound, the solution of which was generally supposed to be incapable of dyeing without the intervention of an acid. The author, however, states that it is merely necessary, after having immersed the substance to be dyed in the ammoniacal solution, to raise the temperature of the latter gradually, without boiling; the material is thus dyed a brilliant red, while the solution remains as at first, perfectly colourless. In explanation of this phenomenon, he suggests that possibly the weak combination of rosaniline with ammonia is decomposed by heat, and that the wool or other material in uniting with the colourless base, plays the part of an acid, thereby producing the coloured compound. When aniline-blue is substituted for rosaniline, the material, after immersion in the colourless solution, will become blue merely on exposure to air.

J. W.

**On Crystallised Hyoscyamine.** By THIBAUT (Chem. Centr., 1875, 565).

THE hyoscyamine prepared by the author had no resemblance whatever to commercial hyoscyamine, and had a totally different smell; but during the preparation a substance was noticed having the same smell

as the commercial article, and the author consequently believes that there are two different alkaloïds present in henbane.

H. H. B. S.

**Decomposition of Atropine in Contact with Putrefying Animal Substances.** By F. SELMI (Deut. Chem. Ges. Ber., ix, 347).

THE products differ according as the decomposition takes place in acid or in ammoniacal masses; and the decomposition by means of baryta differs from that effected by ammonia. It was not found possible to isolate small quantities of atropine giving the characteristic reactions of the alkaloid, or to obtain crystalline products with iodated hydriodic acid or picric acid. But atropine could still be recognised by the odour of hawthorn-blossom emitted on evaporation in the air, which odour is not perceptible when oxygen is excluded. The intensely bitter ethereal extract was poisonous, and caused expansion of the pupils.

J. R.

**On Pittacal.** By C. LIEBERMANN (Deut. Chem. Ges. Ber., ix, 334—337).

THE high-boiling portion of wood-tar yields, by a process of oxidation which has not yet been published, a brown earthy substance, soluble in alkalis with blue colour, but containing only a small percentage of colouring matter. This colouring matter has been isolated by the author by digesting the brown substance with hot acetic acid, mixing the filtered solution with excess of neutral lead acetate, treating the resulting precipitate with hydrogen sulphide, and exhausting the washed lead sulphide with warm alcohol, which dissolves the colouring matter, and leaves it on evaporation as an orange-red crystalline powder.

The colouring matter is soluble in alcohol and acetic acid, with brown colour. Alkalis dissolve it with purple, ammonia with blue colour, forming solutions from which carbon dioxide throws down blue salts, soluble in pure water. In the alkaline solutions calcium, magnesium, barium, and tin salts produce blue precipitates, often having a beautiful golden lustre. The calcium and magnesium precipitates are soluble in pure water. Hydrochloric and strong sulphuric acids dissolve the substance with red colour: the latter solution turns pure blue on warming. The pure orange-coloured substance acquires a deep golden lustre when moistened with strong mineral acids. In acid solution it dyes animal fibres orange; in ammoniacal solution, especially with tin mordant, blue-violet. The substance is free from nitrogen. It contains, as shown by three concordant analyses, 63·6 p. c. carbon, and 5·6 p. c hydrogen.

This substance is not Reichenbach's pittacal, to which, however, it is closely allied. To distinguish it therefrom the author proposes to call it *cupittone*.

J. R.

**On the Oil of Elaeococca and its Solid Modification produced by the Action of Light.** By S. CLOEZ (Compt. rend., lxxxii, 501—504).

THE action of the more refrangible rays of light causes the neutral liquid oil of *Elaeococca* to solidify into a buttery substance, the melting point of which is 32° higher than that of the oil. When saponified with potash, and acidified with phosphoric acid, this fat decomposes into glycerin, and a mixture of two acids, one solid and the other liquid; they were separated by pressure between bibulous paper. The solid acid was purified by crystallisation from alcohol, and combined successively with potassium, barium, lead, and silver. Instead of acidifying with phosphoric acid, the solution of the potassium salt of the new solid acid, which the author names *margarolic acid*, may be cooled; the potassium salt crystallises out in a nearly pure state, and may be completely purified by recrystallisation from alcohol of 0·85 specific gravity. The acid may be prepared from potassium margarolate by addition of phosphoric acid. Margarolic acid crystallises in rhomboïdal plates; it melts at 48°, is insoluble in water, soluble in ether, carbon disulphide, liquid hydrocarbons, and aqueous alcohol; it rapidly absorbs oxygen, and is converted into a soft transparent body, which gradually becomes hard and assumes a resinous appearance. The acid gains 8·5 per cent. in weight on exposure to air for a fortnight. It may be kept without alteration in a sealed tube, or under water.

The analysis of the acid and of its salts led to the formula $C_{17}H_{20}O_3$ for the acid, and $C_{17}H_{29}O_3R$ for the salts.

On addition of water to the potash salt, an acid margarolate crystallises in small nacreous scales.

The liquid acid, separated from margarolic acid by pressure, is purified by formation of the calcium salt, which is treated with ether, and the portion which has dissolved is decomposed with hydrochloric acid. The author gives it the name *elaeolic acid*. Lead elaeolate is soluble in ether, whereas lead margarolate dissolves. These acids appear to indicate two glycerin ethers in the elaeococca, viz., *elaeolin* and *margarolin*.

The solid product formed by the action of light, gives, when saponified, a mixture of fatty acids, from which one melting at 72° was separated, containing less oxygen than margarolic acid. The author names it stearolic acid. W. R.

**On the Milk-sap of Cynanchum Acutum.** By A. BUTLEROFF (Liebig's Annalen, clxxx, 349—355).

THE author has examined a small specimen of this sap brought from the vicinity of the Oxus, where the plant (a creeper belonging to the *Apocyneæ*) is regarded as very poisonous, and especially dangerous to camels. The sap, as it reached the author, consisted of a white, soft, resinous mass, and an aqueous, nearly colourless, liquid, these being probably formed by coagulation of the sap. It had a faint disagreeable odour, somewhat resembling that of infusion of tobacco.

The fluid portion of the sap deposited on evaporation a quantity of potassium chloride free from sodium chloride. The syrupy mother-liquor was treated with alcohol, the alcoholic liquid evaporated, and the residue dissolved in water. A portion of this solution injected into the veins of a dog, exerted no poisonous action. On distilling the solution with potash, there passed over a strongly alkaline liquid of peculiar odour, likewise without poisonous action on a frog.

The white coagulum formed a soft resinous mass. When heated it melted and burned with the smell of burning caoutchouc. The coagulum was treated with alcohol, which dissolved the greater part: the residue dissolved almost entirely in hot carbon bisulphide. The latter solution left on evaporation a transparent yellow, sticky resin, which did not harden in the air, and smelt of burnt caoutchouc when heated. The solution in boiling alcohol deposited on cooling white granules, which, after being purified, crystallised in small needles and shining laminæ. This substance, called by the author *cynanchol*, is moderately soluble in hot, but nearly insoluble in cold alcohol. It is accompanied by an amorphous, resinous body, which appears to hinder its crystallisation.

Cynanchol, when sufficiently pure to crystallise distinctly, is white, bulky, and friable in the fingers. It melts at 135°—145° to a colourless liquid, and on cooling solidifies in a transparent amorphous mass, which becomes white and opaque when moistened with alcohol. It dissolves in alcoholic potash, but is not attacked by it even on heating to 100°. It is not affected by hydrochloric acid or ferric chloride, nor by potassium, bichromate, and sulphuric acid. Strong sulphuric acid colours it reddish-brown in the cold, and blackens it when hot, evolving sulphur dioxide. Nitric acid acts violently upon it, giving off nitrous fumes, and ultimately forming a solution from which water throws down a yellow pulverulent resin, insoluble in ammonia. Analysis of cynanchol leads to the formula $C_{15}H_{14}O$.

J. R.

**Decoloration of Indigo-solution and other Vegetable Dyes by various Sulphur-compounds.** By E. SCHAER (Deut. Chem. Ges. Ber., ix, 340—342).

THE bleaching of indigo-solution by sulphur-compounds, more particularly hyposulphurous acid, $H_2SO_2$, and the hydrogen persulphides ($H_2S_2$ and $H_2S_3$), is generally attributed to the reduction of indigo to indigo-white, a view which derives support from the circumstance that when the bleached solution is shaken with air the blue colour is restored. The author thinks it more probable, however, that the bleaching is due to the formation of molecular combinations of the sulphur-compounds with indigo, whereby the colour of the latter is masked. For a solution of indigo bleached by hyposulphurous acid is turned blue, not only by atmospheric oxygen and all oxidising agents, but also by several reducing agents, especially hydrogen sulphide; and a solution bleached by hydrogen persulphide is turned blue by treatment with gaseous sulphur dioxide or its aqueous solution, as well as by oxidising substances;—facts which admit of easy explanation on

the supposition that hydrogen sulphide in this case acts upon hyposulphurous acid in the same way as upon sulphurous acid, and that hydrogen persulphide behaves like hydrogen sulphide towards sulphur dioxide.

According to this explanation, indigo and other vegetable dyes bleached by hyposulphurous acid or hydrogen persulphide would be restored to their original colours by treatment with any substance which decomposes these sulphur-compounds, and thus sets free the colouring matters.

J. R.

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**Irisol, Oleum Iridis Florentinæ.** By H. HAGER (Chem. Centr., 1875, 688).

THE paper describes various reactions and properties of this substance, which is now prepared on the commercial scale, as a cheap but highly-esteemed perfume, by distilling with water the rhizome of the Florentine iris.

R. R.

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**Hæmoglobin and its Derivatives.** By C. HUSSON (Chem. Centr., 1875, 694).

A NUMBER of reactions of these substances are described.

R. R.

**A few Remarks on Chitin.** By O. BÜTSCHLI (Chem. Centr., 1875, 566).

CHITIN was prepared from lobster shells and purified by boiling with permanganate of potash. The determination of the nitrogen in this substance by Dumas' method showed a somewhat higher percentage than that usually ascribed to it, viz., 7·4 per cent. instead of 6·4 per cent.

Water precipitates chitin unchanged from its solution in hydrochloric or sulphuric acid.

H. H. B. S.

**Researches on the Constitution of Gelatinous Substances.** By A. BOURGEOIS (Compt. rend., lxxxii, 262—264).

THE method of conducting the investigations respecting the constitution of isinglass, ossein, gelatin and chrondrin has been explained in a previous communication. From the proximate analyses of these substances the following results were obtained:—

| | Isinglass. | Ossein. | Gelatin. | Chondrin. |
|---|---|---|---|---|
| Nitrogen as $NH_3$ .... | 3·47 | 3·35 | 2·8 | 2·88 |
| Oxalic acid..... | 4·1 | 3·62 | 3·3 | 4·2 |
| Carbonic acid ..... | 2·5 | 3·1 | 2·72 | 2·45 |
| Acetic acid ..... | 1·5 | 1·44 | 1·5 | 4·69 |

A mixture of amido-compounds also results which, having been submitted to ultimate analysis, was found to be very fairly represented by terms of the series $C_nH_{2n+1}NO_2$ and $C_nH_{2n-1}NO_2$.

The decomposition of isinglass, ossein, and gelatin may, therefore, be approximately expressed in the form of an equation, thus:

$$\underset{\text{Gelatin.}}{C_{76}H_{124}N_{24}O_{29}} + 18H_2O = \underset{\text{Oxalic acid.}}{H_2C_2O_4} + CO_2 + \underset{\text{Acetic acid.}}{0{\cdot}5(H_4C_2O_2)} + 4NH_3 + \underset{\text{Amido-compounds.}}{C_{72}H_{144}N_{20}O_{40}}.$$

The amidated mixture also may be separated in the following manner:—

$$C_{72}H_{144}N_{20}O_{40} = \underset{\text{Glycocine.}}{C(C_2H_5NO_2)} + \underset{\text{Alanine.}}{2(C_3H_7NO_2)} + \underset{\text{Amidobutyric acid.}}{2(C_4H_9NO_2)} + \underset{\text{Terms of the acrylic series.}}{6(C_nH_{2n-1}NO_2)}.$$

The constitution of chondrin appears to be somewhat different. In the mixture of amido-compounds resulting from its decomposition, no glycocine can be detected, but only alanine, amido-butyric acid, the terms $C_4H_7NO_2$ and $C_5H_9NO_2$ of the acrylic series, and some acids of the series $C_nH_{2n-1}NO_4$:

$$\underset{\text{Chondrin.}}{C_{99}H_{156}N_{24}O_{42}} + 18H_2O = \underset{\text{Oxalic acid.}}{C_2H_2O_4} + CO_2 + \underset{\text{Acetic acid.}}{1{\cdot}5(C_2H_4O_2)} + 4NH_3 + \underset{\text{Amido-compounds.}}{C_{93}H_{172}N_{20}O_{52}}.$$

The author thinks that the relation existing between the nitrogen disengaged as ammonia, and the carbonic and oxalic acids produced, is such as to warrant the conclusion that the simultaneous formation of these three bodies is closely associated with the hydration of urea and oxamide.

J. W.

## Physiological Chemistry.

### Ozone and its Action on the Blood. By J. Dogiel (Chem. Centr., 1875, 565).

The author, being prevented by unforeseen circumstances from completing his researches, confines himself to the publication of a short account of the most important results which he has at present obtained, among which are the following:—

Blood is altered very much by the action of ozone, the red corpuscles

being principally attacked; the colouring matter of the corpuscles is thus separated and the blood acquires a darker colour; this takes place in from five to fifteen minutes. By the action of ozone, for a longer time (about an hour), upon previously defibrinated blood, it becomes still darker. Blood thus changed does not deposit crystals of hæmoglobin, even after the addition of ethylic alcohol, ether, or chloroform.

As the blood darkens in colour, it becomes also more viscid, and after this stage a glutinous substance separates in flakes which are shown by the microscope to consist of transparent filaments. This substance, after having been washed many times with water, is not distinguishable by its physical properties from fibrin.

By passing a continued stream of ozone through blood for three or four days, the red colour of the hæmoglobin and hæmatin is changed to a dirty yellowish-green, and the blood finally becomes quite decolorised. The decolorisation proceeds very rapidly if blood largely diluted with water is used instead of the undiluted defibrinated blood.

Defibrinated blood, which has been decolorised by ozone, consists of a colourless fluid and an albuminous substance corresponding in its physical properties with fibrin.

A dog's blood poisoned with carbonic oxide gas acquires in a comparatively short time, by the action of ozone, the characteristics of normal blood; it becomes darker by the action of carbonic acid, and arterial by the absorption of oxygen. Carbonic acid is separated by the action of oxygen on blood poisoned with carbonic oxide.

H. H. B. S.

**The Influence of Temperature on the Metamorphosis of Tissue in the Mammalia.** By E. PFLÜGER (Pflüger's Archiv. f. Physiologie, xii, 282—284).

1. ARTIFICIAL rise or fall of the animal temperature, as measured by a thermometer placed in the rectum, increases or decreases, as the case may be, the consumption of oxygen and excretion of carbon dioxide. With a rectal temperature of 20°, the tissue degradation in mammalia is not greater than in the amphibia.

2. When the nervous system is intact, the depression of temperature in the interior of the animal may more than compensate for the greater activity of the central nervous system brought about by surface cooling; so that, within certain limits, the maximum amount of tissue change will be associated with a high internal temperature, and the minimum change with the lowest internal temperature.

3. Severance of the spinal cord between the sixth and seventh cervical vertebræ brings about a marked diminution, amounting to even one-half, of tissue waste.

4. Section of the cerebral peduncles behind the corpora quadrigemina does not determine any appreciable change in the amount of tissue change.

T. S.

**The Influence of the Eye on Tissue Change in the Animal Body.** By E. PFLÜGER (Pflüger's Archiv. f. Physiologie, xi, 263—272).

OF physiological interest. A theoretical criticism on the researches of many experimenters, and intended as an introduction to the memoir of O. von Platen, already noticed in this Journal.

T. S.

**Human Bile.** By N. SOCOLOFF (Pflüger's Archiv. f. Physiologie, xii, 54).

NOT being able to operate on the bile of recently and suddenly deceased healthy persons, nor on that extracted by means of a fistula, the author had recourse to the contents of the gall-bladders of such patients as did not appear to suffer from any liver-disturbances during their illnesses.

Weighed quantities of bile were evaporated at a not too high temperature, and the residue treated with absolute alcohol until the filtrate was colourless; the alcoholic extract was evaporated to a small bulk and precipitated by means of a large excess of ether; the precipitate was again dissolved in alcohol and precipitated by ether, and the process repeated until the ethereal liquors were colourless; the purified precipitate consisted of sodium and potassium chlorides with taurochloric acid and sodium taurocholate; by determining the percentage of sulphur in this, the amount of bile acids was obtained, no other sulphurised body being present. The alcoholic-ethereal liquors were evaporated to dryness and the residue treated with anhydrous ether; soapy matters were left insoluble, whilst fats, cholesterin, and lecithin were dissolved. The following numbers were obtained as a mean of six analyses of bile from patients dying from *Hæmorrhagia cerebri*, *Nephritis chronica*, *Phthisis pulmonum*, *heart disease*, and *Arteriosclerosis* with *emphysema*, and *acute serous pleurisy*:—

| | Percentage reckoned on fluid bile. | On ethereal precipitate. |
|---|---|---|
| Insoluble in absolute alcohol..... | 3·724 | — |
| Ethereal precipitate ..... | 6·471 | — |
| Sulphur ..... | 0·092 | 1·483 |
| Taurocholic acid..... | 1·490 | 23·833 |
| Sodium taurocholate ..... | 1·567 | 24·725 |
| Soap..... | 1·453 | — |

The amount of ethereal precipitate varied from 3·819 to 9·794 per cent.; other experimenters have obtained varying numbers within about the same limits. The sulphur varied only between 1·130 and 1·677 per cent. of the ethereal precipitate, whence the amount of biliary acids present was approximately constant; similarly the soap fluctuated only between 1·303 and 2·082 per cent. of the bile.

In two cases where the liver was affected, analyses were made with the following results:—(A.) Young woman; died of *Peritonitis puerperalis*: liver much enlarged, and polygonal form of cells lost. (B.)

Man of 40 years; death from amyloïd degeneration of spleen, kidneys, and liver: liver enlarged and showing further fatty degeneration.

| | (A.) | | (B.) | |
|---|---|---|---|---|
| | Reckoned on fluid bile. | On ethereal precipitate. | On fluid bile. | On ethereal precipitate. |
| Insoluble in absolute alcohol .... | 5·253 | — | 1·734 | — |
| Ethereal precipitate ..... | 6·759 | — | 1·316 | — |
| Sulphur ..... | 0·219 | 3·249 | 0·0074 | 0·557 |
| Taurocholic acid ..... | 3·535 | 52·311 | 0·117 | 8·927 |
| Sodium taurocholate ..... | 3·690 | 54·605 | 0·123 | 9·336 |
| Soap ..... | 1·150 | — | 0·260 | — |
| Chlorine ..... | — | — | 0·238 | 18·111 |

In the first case the amount of biliary acids was abnormally high, in the second excessively low; just as would be *à priori* anticipated, since in (A.) the liver was in a state of inflammation, *i.e.*, of much increased activity, whilst in (B.) the opposite was the case. Hoppe-Seyler once investigated a case of fatty degeneration of the liver in which *no trace of biliary acids* could be found in the bile.

C. R. A. W.

## Urobilin in the Urine. By Johannes Esoff (Pflüger's Archiv. f. Physiol., xii, 50—53).

In order to precipitate the body which yields urobilin as a decomposition product, fresh urine is treated successively with neutral and with basic lead acetate; most of the body is thrown down by the former, the rest by the latter; the precipitate is collected and washed and then decomposed by sodium carbonate, or preferably by alcohol and a slight excess of sulphuric acid. The dark-coloured liquid thus obtained is diluted with water and shaken with chloroform as long as the latter takes up colouring matter; the chloroform extract is then filtered and shaken with acidulated water, which again dissolves out some urobilin, leaving, however, the greater part still dissolved in the chloroform together with fats, fatty acids, &c. The acid aqueous liquor is then precipitated with lead acetate, the precipitate decomposed with alcohol and sulphuric acid, and the alcoholic liquor treated with water and chloroform just as at first; the substance left on evaporating this last chloroform solution is not pure urobilin, as it yields to ether a reddish body in some quantity, whilst only a small amount of brown flakes remain insoluble; these exhibit strongly the spectral lines of urobilin when dissolved in alcoholic sulphuric acid. Urobilin is destroyed by both oxidizing and reducing agents; the characteristic lines are no longer shown after treatment with potassium permanganate, lead dioxide, chlorine-water, tin and hydrochloric acid, &c., whilst the syrupy liquid left on evaporating its impure chloroform solution no longer contains it after several months' exposure to air.

Urobilin was detected spectroscopically in normal urine in 4 cases out of 39; in the other 35 instances it could only be found after addition of strong acids, of which sulphuric, nitric and hydrochloric act most energetically in developing the lines, acetic acid being less effective.

C. R. A. W.

**Occurrence of Pyrocatechin in Urine.** By E. BAUMANN (Pflüger's Archiv. f. Physiol., xii, 63—68).

THE dark coloration noticeable in the urine of cattle which has been exposed to the air for one or two days, is due, not to indican, but to the alteration of pyrocatechin and other alteration-products of tannin. This pyrocatechin can be readily extracted by acidulating fresh urine with acetic acid and agitating with ether. The ethereal extract yields on evaporation a brownish resinous mass which is dissolved in water and filtered; the acid liquid thus obtained is treated with a few drops of lead acetate to precipitate colouring matters and resinous bodies; the filtrate from these is carefully neutralized with ammonium carbonate and precipitated with lead acetate; the precipitate is washed and decomposed by sulphuretted hydrogen; the acid filtrate is neutralised with barium carbonate and shaken with ether; and finally, the ether is evaporated, when a residue is left which gives with ferric chloride a deep green colour, becoming a beautiful violet on addition of sodium bicarbonate or ammonia. A concentrated solution gives a greenish-black precipitate with ferric chloride; with soda or ammonia a liquid is obtained which becomes brown by exposure to air; with ammoniacal silver nitrate immediate reduction of silver occurs. As yet the author has not worked a sufficiently large quantity of urine to enable him to obtain the pyrocatechin in sufficient quantity and purity for analysis, but the qualitative tests are so well defined that the presence of pyrocatechin in 200 or 250 c.c. of fresh urine can be readily detected.

Apparently the pyrocatechin is originally contained either wholly or partially as some compound which is insoluble in ether, and is only gradually split up, with formation of pyrocatechin; 200 c.c. of urine, after acidulation and shaking with ether, till no more pyrocatechin is dissolved out, will yield to ether perceptible quantities of pyrocatechin after heating on the water-bath with hydrochloric acid for some time; similarly the urine of a boy twelve years of age gave with ferric chloride no reaction when fresh, but after standing some time and becoming putrid, it yielded with that reagent a dark violet coloration, becoming a dirty green on addition of a drop of acetic acid; on treatment with ether the pyrocatechin reactions were readily obtained from the dissolved substance. This occurrence in urine of pyrocatechin, or of a body yielding similar reactions, has been previously observed by Müller and Ebstein in the case of a healthy child, and by Rajewski in the course of a research on the action of tannin on the organism; the author, however, has failed to find it in the urine of dogs fed on meat, whence apparently vegetable substances are essential to the production of the body.

Hoppe-Seyler has shown that carbohydrates are capable of yielding

pyrocatechin by treatment with water at high temperatures or by the action of alkalis; the author therefore examined various kinds of foods, with the result of finding distinct traces of a body giving the pyrocatechin reactions in various substances, notably in wine, cyder, beer, and saccharine fruits (*e.g.*, apples and grapes, ripe and unripe; potatoes and beets did not yield it). He believed at first that the brown discoloration on the cut surfaces of apples produced by exposure to air is formed by the decomposition of the pyrocatechin, as the green coloration with ferric chloride and the change to violet on further addition of ammonia or sodium carbonate can be readily seen on the application of these reagents to the freshly cut apple itself; but on carefully examining cyder, he found that the colorific body forms a barium salt, and hence is probably either protocatechuic acid (which yields reactions much allied to those of pyrocatechin) or some analogous tannin derivative. Further experiments on this body are in progress.

A liberal addition of fruit to diet did not seem to increase the quantity of pyrocatechin in the urine; on the contrary, the amount was larger when fruit was excluded from the food taken.

C. R. A. W.

**Adipocere.** By EBERT (Deut. Chem. Ges. Ber., viii, 775).

THE absence of glycerin having been ascertained, adipocere was saponified with potash (1 per cent. of ammonia then passing off, and leaving about 6 per cent. of residue, consisting of tissues, &c.) and the method of partial precipitation by magnesium acetate employed. By far the largest quantity consisted of palmitic acid, manganic acid being also present, but in much smaller proportion; this acid had a melting point at 59° (Heintz found 59·9°). The last fraction, which could not be precipitated by magnesia, but gave a precipitate with lead acetate, yielded a colourless crystallisable acid melting at 80°, which was found on analysis to be oxymanganic acid, $C_{17}H_{14}O_3$. This acid is insoluble in water, but soluble in alcohol and ether, forming a white amorphous silver salt, unaltered by light. No oleic acid was detected.

E. W. P.

**The Behaviour of Guanidine, Dicyandiamidin, and Cyanamide in the Organism.** By E. GERGENS and E. BAUMANN (Pflüger's Archiv. f. Physiol., xii, 205—214).

SINCE creatine, which is a substituted guanidine,

$$NH{=}C\begin{cases} N(CH_3)CH_2C.OHO \\ NH_2 \end{cases},$$

appears in the urine as such or as creatinine, the authors thought that guanidine, which readily splits up into urea and ammonia when warmed with caustic alkalis, might possibly also behave in a similar manner. The toxic properties of guanidine are fully described, and offer an impediment to the solution of the problem by the administra-

tion of large doses of that substance, so as to ascertain whether the excretion of urea was thereby increased. The authors were therefore compelled to resort to a direct search for guanidine after its subcutaneous injection. Traces only of it were thus detected. Operating in a similar manner with dicyanodiamine and cyanamide, appreciable quantities of the former were discovered in the urine, but none of the latter substance. T. S.

**Action of Cold on Milk.** By EUG. TISSERAND (Compt. rend., lxxxii, 266—268).

NUMEROUS experiments have been made by exposing milk to different temperatures varying from 0° to 36°, and the following facts have been elicited:—

1. The rise of the cream is the more rapid as the temperature to which the milk is exposed approaches to 0°.
2. The volume of the cream is greater when the milk has been efficiently cooled.
3. The yield of butter is also greater when the milk has been exposed to a very low temperature.
4. Finally, the skimmed milk, the butter, and cheese are of better quality when prepared under the above circumstances.

While it is impossible to offer a satisfactory explanation as to the reason why artificial cold should exert a beneficial effect upon the yield and quality of the products derived from milk, it is probable that it may tend to arrest that fermentative decomposition which is so prone to set in with organic liquids, and thus by preventing incipient alteration indirectly to improve the quality of the material.

The practice of warming the dairy in winter time, so as to maintain its atmosphere at a constant temperature of 12° or 13°, is therefore objectionable; the pans should rather stand in running water at as low a temperature as can be practically obtained. It is further suggested that the foregoing facts should be brought prominently before the notice of those who are engaged in the manufacture of dairy-produce, in order that the many erroneous notions on this subject may be gradually eliminated.

J. W.

## Chemistry of Vegetable Physiology and Agriculture.

**On Chlorophyll.** By F. FILHOL (Chem. Centr., 1875, 542).

THE author has already shown that solutions of chlorophyll undergo a remarkable decomposition when acted upon by small quantities of hydrochloric acid or by larger quantities of certain organic acids. The original green colour disappears, and on filtering, a dark-coloured matter is separated whilst the filtrate appears yellowish-brown. By a further addition of hydrochloric acid, the filtrate acquires a deep-green colour, and on again filtering, a yellow matter is left behind, the filtered

liquid appearing blue. These appearances can be produced with the most different plants, but the black matter obtained from dycotyledons is amorphous, whilst that from monocotyledons appears crystalline. Spirits of wine of 85 per cent. has scarcely any action upon this substance when cold, but it dissolves it readily on boiling. Ether, benzene, chloroform, bisulphide of carbon, and acetic acid dissolve it easily in the cold. Concentrated hydrochloric and sulphuric acids dissolve the crystalline substance slowly. The solutions with ether, benzol, chlorform, &c., are changed by the action of sunlight, and finally quite decolorised. The acetic acid solution aquires a magnificent green colour on heating with a trace of acetate of copper or acetate of zinc, and this explains the formation of the fine green colour which certain condiments acquire on treatment with vinegar and copper.

H. H. B. S.

**Growth of Plants Destitute of Chlorophyll.** By BOUSSINGAULT (Compt. rend., lxxxii, 939).

Two grains of *Helianthus argophyllus* were placed in sand previously calcined and watered with distilled water; potassium nitrate, basic phosphate of calcium, and white siliceous ashes from meadow hay were also added. In 92 days the stalks, leaves, and flowers of the two plants were equal in size and vigour to those of similar plants grown in a garden plot and sown at the same time.

The author discusses how far the solar action is essential to vegetable life, pointing out that even in such cases as the growth of the *Mycoderma aceti* and fungoïd growths which appear in solutions of tartaric acid and various salts, &c., the sugar, tartaric acid, albuminoïds and other analogous bodies essential to the formation of the non-chlorophyllic plants have been originally formed by the agency of sunlight on chlorophyllic plants, and hence he concludes that in the absence of solar radiation *all* vegetation would disappear from the surface of the globe.

Pasteur thinks on the contrary that certain low forms of vegetable life might still continue to flourish. As to whether cell-growth of any kind could go on in the absence of sunlight it is impossible to say, inasmuch as every existing cell owes its origin to a preceding cell. Whether the first primeval cell was formed with or without the intervention of light we know not.

Boussingault rejoins that the observed rule as to the physiological aspect of the question is, that when a low form of vegetable life continues in the absence of sunlight (*e.g.*, the *Mycoderma aceti*) it flourishes only by consuming and altering products derived from substances which owe their origin to the action of light on chlorophyll; thus the vinegar fungus consumes alcohol, which is derived from sugar, which again cannot be formed by plants without the help of chlorophyll and sunlight.

C. R. A. W.

**Exhalation of Water-vapour by Plants.** By K. EDLER (Chem. Centr., 1875, 760).

THIS paper contains the results of an extensive series of experiments on the evaporation of water through different plant-tissues, the exhalation of water vapour by leafless twigs, the behaviour of the watery parts of plants in this respect, and on the circumstances which affect the performance of this function by plants generally.

H. H. B. S.

**Absorption of Bicarbonates from Natural Waters, by Plants.** By A. BARTHÉLEMY (Compt. rend., lxxxii, 548).

THE following abstract is given by the author :—

1. Plants possess one set of roots for the absorption of gas, and another set for the absorption of mineral substances in solution.

2. There are two distinct periods in the life of the roots; of development, previous to the decrease of the bud; and of maturity, when the spongiole, laid bare by the exfoliation of the epidermic tissue, exhibits the phenomena of osmose.

3. Plants absorb more water than bicarbonates from natural waters, except when the leaves dry rapidly, or at the time of flowering.

4. The amount of bicarbonates absorbed is proportional to the amount of exhaled water.

5. In a water of constant composition, plants appear, during the night, to part with some of the bicarbonates absorbed during the day, while absorption of water takes place.

6. The relation of the bicarbonate to the water absorbed, varies with the nature of the plant.

7. When a plant has absorbed a certain amount of bicarbonates, it is able to part with some when placed in distilled water.

8. The absorption of bicarbonates has no direct relation with the rapidity of vegetation; this absorption therefore does not aid respiration.

9. The roots of plants reject the carbonic anhydride which serves to keep the bicarbonates in solution.

10. These experiments made on healthy plants, coincide in a number of points with those made with concentrated solutions and porous vessels.

W. R.

**Gas in Fruits.** By H. STRUVE (Deut. Chem. Ges. Ber., ix, 501).

WHEN young vine-leaves are treated with ether in an appropriate apparatus, a more or less abundant evolution of gas takes place. As the leaves become more developed the phenomenon is less marked, and in autumn it ceases altogether. Grapes similarly treated give off no gas. But when grapes immersed in water are placed under the receiver of an air-pump, and the air is gradually exhausted, an escape of gas from the fruit is observed, ceasing, however, when the pumping is stopped. On resuming the exhaustion after some hours, a more

abundant emission of gas takes place. The gas is entirely absorbed by baryta-water. The evolution goes on for a long time—even for weeks—and provided the experiment is carefully conducted, the grapes do not burst, though they swell a little, owing to osmose. After the experiment the water contains traces of alcohol, with yeast-cells, but no yeast is found in the interior of unburst grapes.

J. R.

### Absorbing Power of the Soil.

By EUG. DURRWELL (Bull. Soc. Chim. [2], xxv, 202).

THE author is able to corroborate Salmonoff's statement that it is the purely mechanical action of irrigation, which distributes the nutritive matters in the soil, and not "a faculty of absorption which permits the uniform distribution of the nutritive matters round the particles of the soil by slow saturation."

C. H. P.

## Analytical Chemistry.

### The Determination of very Small Quantities of Arsenic present in Mineral and Organic Substances. By M. CROMMYDIS (Bull. Soc. Chim. [2], xxv, 348—349).

THE author considers all the methods usually employed in the determination of small amounts of arsenic, to be either inconvenient or inaccurate; and gives the preference to the method first proposed by Gautier, which consists in evolving the arsenic from a Marsh's apparatus in the form of arseniuretted hydrogen, and weighing the metallic arsenic obtained in the combustion-tube. As evidence of the extreme accuracy of this method, the following results are given:—

Orpiment of absolute purity was taken:

| Wt. of orpiment taken. | Metallic arsenic found. | Metallic arsenic calculated. |
|---|---|---|
| 0·0108 | 0·0065 | 0·00658 |
| 0·0052 | 0·0030 | 0·00308 |

On determining the arsenic in a portion of the same sample of orpiment by the ammonium-magnesium arsenate method, inaccurate results were obtained, as will be seen from the following—

| Orpiment taken. | Ammonium magnesium arsenate obtained. | Arsenic found. | Arsenic calculated. |
|---|---|---|---|
| 0·55 | 0·8755 | 0·344 | 0·3353 |

Gautier's method is equally accurate when applied to the determination of arsenic contained in large quantities of organic matter. Known volumes of a standard orpiment solution (0·5 gram of orpiment

dissolved in 1 litre of water) were introduced into 100 grams of meat, and the amount of arsenic determined. The results are given below—

| Wt. of meat taken. | c.c. of solution taken. | Wt. of orpiment. | Wt. of arsenic obtained. | Arsenic calculated. |
|---|---|---|---|---|
| 100 grams. | 5 | 0·0025 | 0·0015 | 0·00152 |
| ,, ,, | 10 | 0·0050 | 0·0030 | 0·00301 |
| ,, ,, | 5 | 0·0025 | 0·0015 | 0·00152 |

It is necessary, however, to abstain from carrying on the carbonisation of the organic matter too far, as it is found that the greater part of the arsenic remains in the charcoal as sulphide. In order to be quite certain that all the arsenic is in solution, the organic matter which has been successively treated with nitric acid, sulphuric acid, and again with nitric acid, is calcined; the residue treated again with a small quantity of nitric acid; and the solution evaporated down, but not calcined. By this process all the arsenic is obtained, and no sulphide remains in the charcoal.

C. A. B.

**On the Influence of Silicic Acid on the Estimation of Phosphoric Acid by Ammonium Molybdate.** By E. H. JENKINS (J. pr. Chem. [2], xiii, 237—239).

THE presence of silicic acid does not interfere with the result; and therefore it is unnecessary to remove it before adding the molybdate.

G. T. A.

**Employment of Electro-Metallurgy in Assaying.** (Chem. Centr., 1875, 527).

THE process for the determination of copper and nickel by electrolysis has been considerably simplified by the employment of a thermo-electric pile instead of the Meidinger elements, which are not constant and often out of order when required for use. The thermo-pile is heated by gas, and no alteration in the strength of the current is observable after three weeks' action; it is in fact affected only by the fluctuations in the pressure of the gas.

H. H. B. S.

**Estimation of Nitrogen in Organic Substances.** By A. DUPRÉ (Bull. Soc. Chim. [2], xxv, 244—248).

THE method consists in a modification of that of Dumas. The substance is heated with cupric oxide, and the evolved gases are made to pass over heated copper contained in the anterior part of the combustion-tube (from which the air has been removed by a current of carbonic acid from a generator), and are collected in a bottle filled with caustic potash.

This bottle has near the bottom two lateral openings, through one

of which the evolved gases are collected, the other being connected with a second bottle, likewise containing caustic potash, by a caoutchouc tube about two feet long. The second bottle serves to completely fill the first before commencing a combustion, by simply raising it above the level of the first or collecting bottle.

The neck of the collecting bottle is fitted with a tube-stopper ground in, and provided with a tap, the prolongation of the stopper above the tap fitting into a basin containing water, through the bottom of it, just as the exit pipe of a gas-holder fits into the water-tray above it. In the performance of a combustion, the collecting bottle is completely filled with caustic potash, the tap in the stopper of the collecting bottle shut, and the supply of carbonic acid cut off. The substance is then heated, and the gases pass into the collecting bottle, the apparatus being finally swept by again passing the current of carbonic acid. The collecting bottle is then shaken to complete the absorption of the carbonic acid, and the nitrogen is collected in a measuring tube by filling the latter with water, inverting it over the orifice of the tube-stopper of the collecting bottle in the water contained in the basin above it, and opening the tap.

The bulk of the nitrogen is read off with the usual precautions.

C. H. P.

## A Modification of Böttger's Sugar Test. By E. Brücke (Chem. Centr., 1875, 733).

The author's method is grounded on the fact that potassium-bismuth iodide precipitates albumin and allied substances.

The double iodide is prepared by dissolving recently precipitated basic bismuth nitrate in a hot solution of potassium iodide with addition of hydrochloric acid.

The liquid to be tested (say urine) is acidified with not too much hydrochloric acid; the reagent is added in excess, and the precipitate which forms is separated by filtration.

The filtrate should not be rendered cloudy by a drop of dilute hydrochloric acid, nor by a drop of the reagent. To the filtrate excess of a concentrated solution of caustic potash is added, whereby white bismuthous hydrate is precipitated. The liquid containing the white precipitate is boiled for some time, and is then examined for particles of reduced metallic bismuth.

If there be a considerable quantity of bismuthous hydrate precipitated, it is preferable to pour the supernatant liquid, together with a small quantity of the precipitate only, into another vessel, and then to boil the liquid.

In order to make sure that the black powder which may be obtained in testing is really metallic bismuth, it is collected on a small filter, washed, placed in a little porcelain dish, and treated with a little hydrochloric acid: the porcelain dish is covered with a well-fitting cover, on the inner surface of which is a small piece of paper moistened with a drop of lead solution.

If the black powder consists of bismuth sulphide, the little piece of

paper will be blackened, but if it be metallic bismuth, no blackening will ensue.

M. M. P. M.

**Volumetric Estimation of Astringent Principles.** By F. JEAN (Compt. rend., lxxxii, 982—984).

TANNIC and gallic acids, and other astringent substances, after the addition of an alkaline carbonate, energetically absorb iodine from its solution, and this absorption takes place in direct proportion to the quantity of the astringent matter present. For the estimation of such substances the author employs a 0·4 per cent. solution of iodine in potassium iodide, and this is titrated by means of a standard solution of tannin in sodium carbonate. Under the influence of the iodine, the tannin solution acquires an intense orange-red colour, which would prevent the starch test being applied as indicator of the presence of free iodine if this test were employed in the ordinary way. But the author rubs powdered starch over white filter-paper, and when a minute drop of the deeply-coloured liquid is placed on the paper, it is instantly absorbed, while the characteristic violet stain due to the free iodine remains. As decoction of oak-bark is found to contain no principle other than tannin, which is capable of exercising this action on iodine, the method is directly available for testing barks intended for tanning purposes.

R. R.

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**Determination of Pepsin.**
By P. GRUTZNER (Chem. Centr., 1875, 824).

SEVERAL test-glasses of equal thickness are filled with a solution of carmine in ammonia, and diluted to 1 per cent. with glycerin. This solution is then diluted with water, 0·1 c.c. with 19·9 c.c., 0·2 with 19·8 c.c., &c. Comparison can be made only when a portion of fibrin remains still undissolved.

E. W. P.

**Modification of the Method for the Detection of Bile-pigment.** By E. FLEISCHL (Chem. Centr., 1875, 568).

IN testing for bile-pigment according to Gmelin's original reaction, instead of adding nitric acid containing nitrous acid, it is now customary to mix the fluid with pure boiled nitric acid, and then cautiously pour some concentrated sulphuric acid to the bottom of the test-tube (Brücke's modification). This is an improvement upon the older method, because the reaction gradually spreads upwards from the line of union of the two fluids, instead of taking place simultaneously throughout the liquid. On account of the high specific gravity of the sulphuric acid, the two liquids mix together very slowly, and thus all the different colours can be seen above one another. The boiling of the nitric acid every time immediately before testing can be dispensed with by employing, instead of free nitric acid, a con-

centrated solution of sodium nitrate. This salt alone has no action whatever upon the bile-pigment, and by its adoption plenty of time is allowed for pouring in the sulphuric acid to the bottom of the tube; the reaction also takes place less violently and disappears more slowly than with pure nitric acid, the colours remaining easily for a half-an-hour or more.

H. H. B. S.

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## Detection by Chemical Means of Various Fibres in Threads and Stuffs. By M. Pinchon (Chem. Centr., 1875, 703).

| Treatment with Solution of Potash or of Soda. | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| The whole dissolves | Zinc chloride | Dissolves the whole in the cold. | The alkaline solution is not blackened by addition of lead-salts. | | | | | | Silk. |
| | | Partial action or none. | Partly soluble. | The insoluble portion is, and the soluble portion is not, blackened by salts of lead. | | | | | Silk and wool. |
| | | | Insoluble. | Blackened by salts of lead. | | | | | Wool. |
| | | Dissolves nothing. | Chlorine-water, and afterwards ammonia. | The fibres coloured red-brown. | Nitric acid turns these fibres red. | | | | Phormium. |
| | | | | No coloration. | The fibres are dyed by alcoholic solution of fuchsine (1 : 20), and the colour is not removed by washing. Potash imparts a yellow colour. | Iodine and sulphuric acid colour | Yellow. | | Hemp. |
| | | | | | | | Blue. | | Linen (flax). |
| | | | | | Fuchsine imparts a colour which can be removed by a washing. Potash does not colour yellow. | | | | Cotton. |
| A portion dissolves, and the thread is attacked. | Zinc chloride | Dissolves a portion. | A part is blackened by lead-salts. | Potash-solution dissolves fibres insoluble in zinc chloride: and those which resist this second treatment are soluble in ammonio-cupric solutions. | | | | | Wool, silk, and cotton. |
| | | | No blackening by lead-salts. | Picric acid dyes one part yellow; the other part remains white. | | | | | Silk and cotton. |
| | | Dissolves none. | Nitric acid colours a part yellow; the other part remains white. | | | | | | Wool and linen. |

R. R.

# Technical Chemistry.

**On certain Circumstances which affect the Purity of Water supplied for Domestic Purposes.** By M. M. PATTISON MUIR (Chem. News, xxxiii, 102, 125, 145, 167).

THE action of metallic pipes and vessels and of house cisterns upon potable waters is considered in this paper. Measurements of the solvent action upon lead and upon copper of water containing various salts in solution are given. It is shown that nitrates increase this action in a marked degree, while carbonates diminish it; that the action is almost *nil* when copper is the metal acted upon (the experiments are detailed only for small surfaces of copper exposed); that the presence of carbon dioxide in water, especially when that gas is forced in under pressure, materially increases the solvent action of that water upon both lead and copper.

It is further shown that in ordinary house cisterns the water is not contaminated to any great extent with sewer gases, but that if such water be allowed to remain undisturbed in a cistern it soon shows symptoms of contamination. Numerous experimental details are given.

M. M. P. M.

**Formation of Sulphuric Anhydride by the Combustion of Pyrites.** By F. BODE (Dingl. polyt. J., ccxviii, 322—328).

SCHEURER-KESTNER (*Bull. Soc. Chim.*, 1875, xxiii, 437, and *Chem. Soc. J.*, 1875, 1237) states that the formation of sulphuric anhydride by the combustion of pyrites arises from the oxidation of the sulphurous anhydride in presence of ferric oxide. Wöhler, however, long before Kuhlmann (to whom Scheurer-Kestner refers), directed attention to the property which ferric oxide possesses of causing other bodies to absorb oxygen when heated, and Plattner showed, 20 years ago, that sulphurous acid is converted into sulphuric acid in the presence, not only of ferric oxide, but of a whole series of other bodies. Scheurer-Kestner concludes from his experiments that the sulphuric anhydride obtained in the roasting process could not have been formed by the decomposition of sulphurous acid; but Plattner remarks that although the experiments made seem to confirm this view, it may still be supposed that, under certain conditions, the sulphurous acid formed by oxidation of sulphides absorbs the oxygen of the metallic oxides formed at the same time, and thus becomes converted into sulphuric acid. The author does not wish to enter minutely into Plattner's investigations, and merely refers to the book of this excellent metallurgist to show that the question of the formation of sulphuric anhydride by the combustion of pyrites has already been answered and completely exhausted.

Scheurer-Kestner further thinks that the presence of sulphuric acid in the burnt gases explains also to some extent the amount of oxygen

which is missed when the gases are examined near their entry into the first chamber, the acid having already been condensed in the gas conduit. He gives the following gas analysis:—

| | |
|---|---|
| Sulphurous anhydride.... | 4·34 |
| Oxygen..... | 11·18 |
| Nitrogen ..... | 84·48 |
| | 100·00 |

From the quantity of sulphurous acid the composition of the gas mixture is calculated, by supposing that the oxygen of the air is used merely for the formation of sulphurous acid and ferric oxide, giving—

| | |
|---|---|
| Sulphurous anhydride.... | 4·34 |
| Oxygen..... | 15·41 |
| Nitrogen ..... | 80·25 |
| | 100·00 |

results with which the author cannot agree. As the sulphurous anhydride takes up the same volume as the oxygen required for its formation, and as the oxygen in the atmospheric air is equal to 20·96 per cent., the oxygen-residue must amount to 20·96 − 4·34 = 16·62, and the theoretical composition would be—

| | |
|---|---|
| Sulphurous acid ..... | 4·34 |
| Oxygen..... | 16·62 |
| Nitrogen ..... | 79·04 |
| | 100·00 |

Scheurer-Kestner could not obtain satisfactory results by the direct determination of the proportion of sulphurous anhydride to sulphuric anhydride in the burnt gases. In order to obtain results agreeing with the gas analysis, Bode advises also to determine the sulphuric anhydride in the burnt ore, and not to be satisfied with the determination of the burnt gases. But even then one inaccuracy still remains unnoticed, namely, in the fact that part of the sulphuric acid is combined not with ferric but with ferrous oxide, which again requires less oxygen for its formation than ferric oxide.

D. B.

**Composition of the Gases obtained by Burning Pyrites.** By SCHEURER-KESTNER (Bull. Soc. Chim. [2], xxv, 168—174).

IN answer to Bode's criticism (*Dingl. Polyt. J.*, ccxviii, 322), the author says that he is quite aware of the fact that other chemists have detected the presence of sulphuric acid in the gaseous products of the combustion of certain metallic sulphides, and that he should have been glad of having published his experiments, even if they had had no other result than to draw the attention of manufacturers to the considerable amount of sulphuric acid found in the gases. Some time

ago he had occasion to refer to Plattner's book, and found his experiments mostly to agree with those of this famous metallurgist, excepting as to one fact, viz., the formation of sulphuric anhydride by passing sulphurous anhydride (dried and freed from air) over red hot oxide of iron.

Bode in the second part of his criticism tries to prove, without relying on any experiment of his own, that a considerable mistake has been made in the calculation of the author's gas analysis. In reply to this, Scheurer-Kestner points out that Bode in his determination commits a great error by forgetting that the oxygen is consumed not only in the oxidation of the sulphur, but that a certain quantity is absorbed also by the iron to form ferric oxide.

Four volumes of sulphurous anhydride are formed at the expense of the pyrites and of 11 volumes of oxygen—

$$FeS_4 + O_{11} = FeO_3 + 4SO_2.$$

Of the 11 volumes of oxygen, three combine with the iron and eight with the sulphur; thus 2 volumes of oxygen are required to form 2 volumes of sulphurous acid. For the formation of the oxide of iron 75 volumes of oxygen are required. We therefore obtain for 4·34 $SO_2$ the proportion—

$$2 : 0{\cdot}75 :: 4{\cdot}34 : 1{\cdot}62,$$

*i.e.*, 1·62 of oxygen have been absorbed by the iron, and we have—

| | |
|---|---|
| $SO_2$ ..... | 4·34 |
| O and N ..... | 95·66 |
| | 100·00 |

but as soon as the gases escape from the furnace, they have already lost the oxygen absorbed by the iron, viz., 1·62. We thus obtain—

| | |
|---|---|
| $SO_2$ ..... | 4·34 |
| O and N as above ..... | 95·66 |
| O absorbed by the iron.. | 1·62 |
| | 101·62 |

As air contains 21 per cent. of oxygen, the 101·62 parts are equal to 21·34 per cent. If we deduct from this 4·34 + 1·62, *i.e.*, the quantities necessary for the formation of the $SO_2$ and those absorbed by the iron, we obtain the quantity of oxygen belonging to the gas after it escapes from the furnace—

$$21{\cdot}34 - 5{\cdot}96 = 15{\cdot}38,$$

a number agreeing very well with that given in the original gas analysis.

The composition of the gas will therefore be—

| | |
|---|---|
| Sulphurous anhydride .. | 4·34 |
| Oxygen ..... | 15·38 |
| Nitrogen ..... | 80·28 |
| | 100·00 |

As these corrections are of little importance, the author had confined himself to calculate what would have been the composition of the gas containing 4·34 per cent. of sulphurous anhydride if there had been no deficiency of oxygen.

The quantity of metallic sulphates found in the residues is only a very slight one, contrary to that found by Bode, only about 1½ to 2 per cent. of sulphur. By taking the highest number, 2 per cent., and by supposing the iron to be entirely in the form of sulphate, we find that the quantity of oxygen which might have been absorbed by the formation of this sulphate amounts to only 0·35.

In the conclusion of his paper, Bode advises the determination of the sulphuric acid, not only in the gaseous products, but also in the residues. The author agrees to this, and further adds that ferrous sulphide is another substance likely to be present.

D. B.

## Removal of Arsenic from Sulphuric Acid. By R. Wagner (Dingl. polyt. J., ccxviii, 321).

The author thinks that sulphide of sodium ($Na_2S$) would be preferable to hyposulphite (thiosulphate) of sodium for the purification of chamber acid, and although the acid when purified by either of these reagents, always contains ⅓ of a per cent. or more of sodium sulphate, yet the results and expenses seem most satisfactory by using the former. Dupasquier's method based on the addition of barium sulphide to chamber acid of 50° B., seems to be the best if the sulphate of sodium is objected to. Thiosulphuric acid, however, will always be a very valuable agent in the purification of acid, the barium compound being more suitable than the sodium compound. The following equation shows the reaction:—

$$3(BaS_2O_3 + H_2O) + As_2O_3 = As_2S_3 + 3(BaSO_4) + 3H_2O.$$

19·8 parts of arsenious acid require 85·5 parts of thiosulphate of sodium of the formula ($BaS_2O_3 + H_2O$).

D. B.

## Manufacture of Superphosphates for Agricultural Purposes. By A. Maillet (Compt. rend., lxxxii, 522—524).

When superphosphates are prepared by treating precipitated calcic phosphate with sulphuric acid, all the tricalcic phosphate is not decomposed, but some remains to be acted on during the process of drying, by the liberated phosphoric acid, and some dicalcic phosphate is formed. Spanish apatite, however, does not yield the latter salt, but, with sufficient sulphuric acid to decompose the calcium carbonate and fluoride, it is wholly converted into superphosphate. With green coprolites a retrograde action proportional to the amount of sulphuric acid used takes place after about two years, and ferric phosphates are formed. If too little sulphuric acid is employed, the restored phosphate consists of a mixture of iron phosphate and di-

calcium phosphate. The alumina is never attacked. Phosphates from Quercy, which contain iron and aluminium, also undergo a retrograde action, the phosphoric acid combining with the iron and aluminium to form insoluble phosphates, but very little dicalcic phosphate is formed. Phosphorites from Lot, which are poor in phosphates, form a pasty mass on treatment with sulphuric acid, owing to the large quantity of alumina which they contain. The aluminium phosphate becomes insoluble after some time, and there is a considerable retrograde action. This retrograde action may in general be ascribed to the presence of sesquioxides, and especially ferric oxide, whether it originally, as in the case of the green coprolites, exists as ferrous, or as ferric oxide.

W. R.

**Composition of Gas-lime.** By A. GUYARD (HUGO TAMM) (Bull. Soc. Chim. [2], xxv, 103).

THIS gas-lime was obtained from the same London works, the gas-lime of which has been analysed by Graham:—

| | Guyard. | Graham. |
|---|---|---|
| Calcium hydrate | 15·10 | 17·72 |
| Calcium carbonate | 24·20 | 44·48 |
| Calcium sulphate | 0·25 | 2·80 |
| Calcium sulphite | 1·50 | 14·57 |
| Calcium sulphide | 6·90 | — |
| Calcium oxysulphide | 3·20 | — |
| Calcium hyposulphite | 11·80 | 12·30 |
| Calcium cyanide | 0·25 | — |
| Iron sulphide | 0·55 | — |
| Sulphur | 4·30 | 5·14 |
| Silica | 1·80 | 0·71 |
| Alumina | 0·70 | — |
| Magnesia | traces | — |
| Tar | 0·25 | — |
| Water | 19·20 | 32·28 |

The sample analysed by the author was not exposed to the air, but Graham's probably was.

C. S.

**Analysis of a Residue from the Manufacture of Sodium.** By A. GUYARD (Bull. Soc. Chim. [2], xxv, 102).

THE sodium was prepared by using—

| | |
|---|---|
| Soda-ash | 56·5 |
| Oil | 18·5 |
| Coke | 10·5 |
| Chalk | 14·5 |

The residue, after being exposed to the air, consisted of—

| | |
|---|---|
| Soluble portion (dried) | 35 |
| Water | 9 |
| Carbon | 22 |
| Calcium carbonate and oxysulphide with a little alumina | 18 |
| Ashes and oxide of iron | 15·4 |

The soluble proportion gave the following results:—

| | |
|---|---|
| Caustic soda | 11·90 |
| Sodium carbonate | 44·30 |
| Sodium sulphate | 24·10 |
| Sodium sulphite | 11·70 |
| Sodium sulphide | 0·45 |
| Sodium chloride | 7·05 |
| Silica | 0·20 |
| Alumina | 0·30 |
| Lime and potash | small traces. |

C. S.

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## Extraction of Silver by the Moist Way.

By A. Guyard (Bull. Soc. Chim. [2], xxv, 99—102).

Round the great Salt Lake enormous deposits of spongy silica are found, which evidently were deposited from hot springs. These deposits contain lead oxide, cupric oxide, ferric hydrate, ferric oxide, and silver chloride in varying proportions. The quantity of the latter is 1—10 kilograms per ton, but as an average 2·3—2·5 kilograms. The great amount of silica, which seldom is less than 90 per cent., makes it impossible to extract the silver by smelting, and it has been found also very difficult to extract the silver chloride by alcaline chlorides or thiosulphates. But the following method gives very good results, not more than 100 grams of silver per ton of ore being lost.

One part of the ore is boiled with 3·5 parts of salt and 3·5 parts of strong hydrochloric acid until the mass is disintegrated, then the same quantity of hydrochloric acid is added, and one part of manganese oxide is gradually introduced. When the evolution of chlorine ceases, the liquid is decanted, the residue washed with water, and from the solution the silver is precipitated by iron. To remove lead and a little copper, it must be refined by cupellation. On working on a large scale, the above proportion will be found sufficient for 2—3 parts of ore. As manganese oxide, pyrites, salt, and coal are plentiful in Utah, this process can be carried out without difficulty.

C. S.

# PAPERS READ BEFORE THE CHEMICAL SOCIETY.

## VII.—*On the Action of Malt-extract on Starch.*

By CORNELIUS O'SULLIVAN.

MUSCULUS (*Bull. de la Soc. Chim.*, xxii, 32) in a paper recently published, agrees with Schwarzer, Payen, and Schultz and Maerker, that when diastase (malt-extract) is made to act on starch-paste under certain conditions, the saccharification stops when it reaches 51 per cent., or, as he takes it, one-half of the matter dissolved. His original impression that only one-fourth of the starch was converted into sugar, he attributes to the varying structure of the starch-granules, one coating offering a greater resistance to the action of the diastase than another. He has given no details of the experiments which led to his corrected notion, nor does he state the method by which the *sugar* was estimated. No doubt he employed the alkaline copper solution, and took the amount of reduction to represent dextrose. This observer still holds that the saccharification of starch under the influence of diastase is a splitting-up of the starch-molecule, attended with hydration, into sugar and dextrin.

Bondonneau (*Compt. rend.*, lxxxi, 1212) concludes that the saccharification of starch is not a splitting-up, but that each starch-molecule must pass through four isomeric modifications, viz.:—

| | | |
|---|---|---|
| Amylogen (soluble starch) | specific rotatory power $[\alpha_D]$ | + 216° |
| $\alpha$-Dextrin | ,, | + 186° |
| $\beta$-Dextrin | ,, | + 176° |
| $\gamma$-Dextrin | ,, | + 164° |

before it arrives at the end-product, *glucose*.

I (*Chem. Soc J.* [2], x, 581) have already demonstrated that soluble starch, $\alpha$-dextrin and $\beta$-dextrin, have all the same specific rotatory power, viz., $[\alpha_j] = 214°$. M. Bondonneau gives no minute account of the method by which he prepared these bodies and determined their angular values; sufficient, however, is stated to enable me to understand clearly wherein his error lies. He prepared them from the commercial dextrin obtained by the action of heat on starch. When I come to describe my examination of this substance, there will be no difficulty in demonstrating that it is a mixture of the dextrins, sugar under certain conditions, and *torrefaction products*. These latter bodies are optically inactive, do not reduce alkaline copper solution,

and are only partially soluble in alcohol; in fact some of them would seem to have all the properties of dextrin with the exception of its optical activity. It will, therefore, be seen how difficult it is to obtain a pure dextrin from this source, and how easy it is to prepare from it mixtures of dextrin or the dextrins with the torrefaction products, varying in optical activity from 214° downwards. In separating the reducing bodies, M. Bondonneau employs cupric chloride and an alkali, and does not seem to consider for a moment the action of the alkali on dextrin, or the difficulty with which the products of the oxidation of the sugars are separated from it by means of alcohol.

I (*Chem. Soc. J.*, xxix, 478) have already shown that M. Bondonneau's $\gamma$-dextrin is the non-reducing power of maltose; in other words, the difference between its reducing power and that of dextrose.

Petit (*Bull. de la Soc. Chim.*, xxiv, 519), being no doubt misled in the same way, calls attention to the presence of a *sugar* amongst the products of the action of diastase on starch which he says is fermentable, does *not* reduce alkaline copper solution, and is soluble in alcohol. He is occupied with the isolation of this body and the determination of its properties. I must leave him to his work and proceed to describe the experiments I have made to determine the quantitative character of the change which starch undergoes in presence of the active agent, diastase, contained in malt-extract, and state the conclusions arrived at.

Hitherto all investigators on this subject have looked upon the amount of reduction of cupric oxide as sugar, taking 2·205 grms. of cupric oxide as the equivalent of 1 grm. of that body, and have considered the remainder of the substance in solution as dextrin.

We now know that 1 grm. of the sugar produced in this reaction does not reduce 2·205 grms. cupric oxide, but $2{\cdot}205 \times 0{\cdot}65 = 1{\cdot}4332$ grms.: hence the difference between the amount of cupric oxide reduced calculated as dextrose and the total matter in solution from the starch, is not dextrin.

With the light thrown by my previous paper upon the properties and compositions of maltose and dextrin, it is sufficiently easy to determine quantitatively in what proportion the bodies are produced; but I must say that the results obtained were for a long time so apparently discordant and contradictory as to make it anything but an easy task to classify them. Various proportions of these bodies were found under apparently like conditions, and at first it seemed impossible to account for the variations; as soon, however, as the character of the change began to be better understood, the causes to which they were attributable became clear.

Although it appears to me unnecessary to describe minutely the experiments by which I have proved that maltose and dextrin are the

only bodies produced when starch is dissolved by malt-extract, it is nevertheless desirable to give some account of the process.

I. *Maltose and Dextrin are the only products of the Action of Malt-extract on Starch.*

100 grms. of purified air-dried potato-starch were gelatinized in the usual way, that is, stirred up with 200 c.c. water at 55°—60°, and, as soon as the granules were thoroughly dispersed through the liquid, 400 to 500 c.c. boiling water were added with continual stirring. In this way an almost transparent and perfectly homogeneous paste was obtained. This was cooled to 60° and the cold extract* of 10 grms. of pale malt added. At the end of five or six minutes the paste was dissolved, the solution was rapidly cooled and then filtered to remove a slight turbidity due to a little flocculent matter from the extract and impurity from the starch. The residue on the filter gave a blue coloration with iodine; the filtrate gave no colour with this reagent, and by a method which I shall describe in detail further on, it was found to contain a substance which gave a reduction of cupric oxide, represented by (*a*) 44 per cent. dextrose, and to have a specific rotatory power $[\alpha_j] = + 170{\cdot}8°$. On being slowly evaporated, the cupric oxide reduced by the solid matter in the syrup represented (*b*) 45·81 per cent. dextrose, the sp. rot. power at the same time diminished to $[\alpha_j] = + 169{\cdot}1°$. If it be supposed that the amount of reduction in both cases is due to maltose, and the remainder be dextrin, we get for

*a.* 44 ÷ ·65 = 67·7 per cent. maltose and 32·3 per cent. dextrin.
*b.* 45·81 ÷ ·65 = 70·5 „ „ „ 29·5 „ „

How do these proportions agree with the optical activity? Let us compare the specific rotatory powers.

| Observed. | Calculated from the maltose and dextrin given above.† |
|---|---|
| $a = 170{\cdot}8°$ | 170·6° |
| $b = 169{\cdot}1°$ | 168·9° |

The close agreement of the observed and calculated activity leaves little doubt of the correctness of the supposition. As the reducing body can, however, be separated from the non-reducing one, it was as well to prove absolutely that the former was maltose and the latter dextrin.

The syrup (*b*) was evaporated as much as possible on a water-bath, with continual stirring towards the end. While still hot it was placed

* By cold malt-extract, I mean the filtered solution obtained by treating finely-ground malt with water at 16°—20°.

† For mode of calculation, see p. 129.

over sulphuric acid under the bell-jar of an air-pump, and the air slowly exhausted; on the first few strokes of the pump it began to swell up to a frothy mass and evolved much water. Care must be here taken, and the air gradually exhausted, or the substance will flow over the sides of the vessel into the acid: the mass must now be allowed to cool a little, and if the evaporation has been carried sufficiently far, the exhaustion can be completed. At the end of a few hours the solid matter obtained was a white, brittle, highly hygroscopic porous mass. This was powdered and boiled with 20 times its bulk of alcohol, sp. gr. 0·83; the insoluble portion became quite syrupy from the absorption of water, and on cooling the alcoholic solution became perfectly clear. This latter was decanted off and submitted to distillation. The syrup thus obtained crystallised on standing for a few days, the whole becoming solid. On analysis, being first dried in vacuo and then at 100°, it was found to reduce cupric oxide as if it contained 66—67 per cent. dextrose, and gave a sp. rot. power $[\alpha_j] = 148°$, the whole of it fermented on being submitted to the action of yeast, and yielded 51·5 per cent. of alcohol. Hence the substance here dissolved is maltose alone, slightly contaminated with a little of the malt-extract which is partially soluble in alcohol.

The residue left on decanting the solution was also analysed. It was found to reduce as much cupric oxide as if it contained 26·66 per cent. dextrose = 41 per cent. maltose: hence 59 per cent. dextrin. The sp. rot. power observed was $[\alpha_j] = + 185·5°$; the number calculated for a mixture containing maltose and dextrin in the proportions found is $[\alpha_j] = + 187·76°$, being 2·26° higher than the observed angle. This is not due alone to the error of manipulation, but in part to the fact that a portion of the malt-extract is insoluble in alcohol.

The syrup was again solidified in the manner described above, and boiled with alcohol. The alcoholic solution was treated as before, and found to contain only pure maltose, reducing the same amount of cupric oxide and having the same sp. rot. power. The portion insoluble gave a reduction of cupric oxide = 24·6 per cent. maltose on the dry substance: hence 75·4 per cent. dextrin. The observed sp. rot. power was found to be $[\alpha_j] = + 197·5°$, the number calculated from the dextrin and maltose would be $[\alpha_j] = + 198·2°$.

On repeating this operation several times with the residue, the alcohol was found to dissolve nothing but maltose, and the insoluble portion to be a mixture of maltose and dextrin, the proportion of the latter gradually increasing with each successive treatment. I have already pointed out the impossibility of completely freeing dextrin from the reducing body by means of alcohol. Repeated experiments proved that the insoluble portion always retains the power of reducing cupric

oxide equal to from 10 to 12 per cent. of maltose, and when this point is reached, it is only with the greatest difficulty that the reducing body can be diminished. If, however, the amount of reduction be calculated as maltose and the remainder of the substance be taken as dextrin, the calculated sp. rot. power of such a mixture was invariably found to agree very closely with that observed. Many of these residues have been analysed. I give the results of a few determinations:

| | Observed sp. rot. power. | Cupric oxide reducing power. | The same calculated as maltose. | Calculated sp. rot. power.* |
|---|---|---|---|---|
| I..... | 204·6° | 9 per cent. | 13·8 per cent. | 205·17° |
| II..... | 205·5 | 8 ,, | 12·3 ,, | 206·13 |
| III..... | 203·7 | 10 ,, | 15·3 ,, | 204·21 |

A comparison of the calculated with the observed numbers in these experiments conclusively establishes that the reduction is due to maltose, and that dextrin is the only other body present. As all that portion dissolved by alcohol was proved to be maltose, the evidence that dextrin and maltose are the only products of the action of diastase on starch under the conditions mentioned is complete; and the same results being obtained under the greatest variety of circumstances, it is impossible to arrive at any other conclusion.

I should not go into such minute details were it not for the diversity of opinion and statement existing on the subject; the same reasons would lead me to give the numbers obtained by the repetitions above mentioned, but without doing so the assertion will be abundantly proved in the sequel.

In this work the determination of—

(a.) The solid matter in a given volume of solution,
(b.) The *cupric oxide reducing power*, and
(c.) The specific rotatory power,

has been of the very first importance. I shall, therefore, have to give a short account of the methods by which results were obtained under each of these heads.

### a. *The total Solid Matter in Solution.*

In working with the carbo-hydrates it is absolutely necessary that we should be able to ascertain accurately what quantities of them exist in a given weight or volume of a solution without evaporating and drying, this process being attended in most cases with much difficulty

* These numbers are calculated as follows:—I gave 13·8 per cent. maltose, hence 86·2 per cent. dextrin: 1 grm. maltose = 15°, 1 grm. dextrin = 21·4°, then (1·38 × 15) + (8·62 × 21·4) = 205·17°.

and under all conditions giving untrustworthy results. If it be possible to prepare the substances in a pure state so that their specific gravity in solution can be determined, we have at once a method by which the desired information can be obtained. I have prepared pure dextrin and pure maltose, and have found, as stated elsewhere, that both have the same specific gravity in solution, namely 1·626, water being unity. This means simply that a solution of either of them containing 10 grms. dry substance in 100 c.c. of solution at 15·5° has a specific gravity of 1038·5, water being 1000; a solution of 1 grm. in 100 c.c. a sp. gr. = 1003·85; and solutions containing intermediate quantities have proportionally intermediate gravities. Hence the number of grms. in 100 c.c. of solution of any specific gravity can be determined by dividing the weight above water by 3·85. For example, a solution of sp. gr. 1003·85 contains 1 grm.; one of sp. gr. 1007·7, 2 grms., and so on; a table can be constructed with these data from which the grms. in 100 c.c. solution of any gravity can be seen. By this method the solid matter in solution in all the experiments to be described in this paper was determined. It is possible that the numbers, as will be seen from some of the determinations themselves, are from 0·5 to 1 per cent. too low; but as I have almost invariably obtained these results with pure dextrin and maltose, I must, for the present, keep this consideration out of the question and adhere to the numbers given. It is no doubt difficult to obtain dextrin or maltose absolutely dry; the presence of 0·5 to 1 per cent. of moisture would account for the difference indicated here if it really exists.

### b. *The Cupric Oxide Reducing Power.*

Before describing the method by which I determined the amount of reduction of cupric oxide, I must explain what I mean by the term "*cupric oxide reducing power*," as I shall have to use it frequently in this work. Dextrose being the type of reducing bodies and the substance for which the amount of cupric oxide reduced was first determined, I use it as the standard to which to refer all other reducing carbo-hydrates or mixtures of reducing with non-reducing ones. I take the cupric oxide reducing power of a body or mixture to be the amount of cupric oxide, calculated as dextrose, which 100 parts reduce. This power then for dextrose would be 100, for maltose 65, for lactose 70, for dextrin 0, a mixture containing equivalent quantities of dextrin and maltose 44.

The alkaline copper solution was made in the usual way (*Fress. Quant. Anal.*, p. 577, 3rd Ed.), 100 c.c. being = ·5 grm. dextrose, but as it was never used volumetrically, it was hardly necessary to be absolutely accurate. Of this solution 25—30 c.c., containing a fairly weighable

quantity of cupric oxide, were taken in a beaker of 130—140 c.c. capacity, and about 50 c.c. boiling, well boiled water added to it. This was then placed in another larger beaker of boiling water, kept boiling on a sand bath over a bunsen. At the end of five or six minutes, when the dilute copper solution acquired as nearly as possible the temperature of the surrounding water, a quantity of the solution to be assayed, containing a known weight of solid matter, was added, and the boiling continued for 12 to 14 minutes. If the blue colour completely disappears in the first three or four minutes, it can be restored by adding quickly more copper solution, but if two or three additions be necessary to ensure an excess, the assay must be thrown away and a fresh start made with less sugar solution. I have found this the most advisable plan, as under any other conditions I could never obtain satisfactory results; finding generally with solutions of maltose or the glucoses, 3 or 4 per cent. less than the true amount; whilst when dextrin was also present the results were correspondingly high. In a few direct experiments in which too large a quantity of sugar solution was taken, and to which three additions of copper solution had to be made within five minutes to ensure an excess, I found 95·8 for 100 of dextrose, and 61 instead of 65 for maltose. Under the same conditions, with a mixture of dextrin and maltose, I obtained 46·5—48 in three experiments, instead of 44.

When the sugar solution contains more than 2 grms. solid matter in 100 c.c., it is necessary to weigh the required quantity, because by taking the burette measurement alone an error of 2 or 3 per cent. can easily be introduced; whilst with a weighed quantity of solution this is impossible.

I have said that the sugar solution should be boiled with the excess of copper solution from 12 to 14 minutes; this time gives the true reduction for dextrose and maltose, and the quantity remains constant even if the boiling be continued for 20 minutes. But if the solution in addition contains dextrin, and the boiling be continued beyond 13—14 minutes, the amount of cupric oxide reduced gradually increases, owing doubtless to the slow conversion of the dextrin. At the end of 13—14 minutes' boiling the cuprous oxide precipitated is rapidly filtered out, washed with boiling well boiled water, dried, and ignited in a porcelain crucible in the usual way. Strong ignition in an open crucible for five or six minutes converts the cuprous oxide completely into cupric oxide, and treatment with nitric acid is unnecessary. One ignition without nitric acid gave 0·325 grm. cupric oxide, and the same treated with nitric acid gave 0·325 grm. Another experiment gave 0·330 and 0·331 grm. respectively. I need not multiply these examples.

These statements are the results of careful observation; I would there-

fore ask any one who has sugar determinations to make, first to estimate the cupric oxide reducing power volumetrically, and afterwards as I have directed, before deciding in favour of either method. Concordant results may with great care be obtained by the volumetrical process, but from long experience I have found them in no way satisfactory. Very little more trouble is involved in the gravimetrical method, and this is amply compensated for by the reliance that can be placed on it.

### c. *The Specific Rotatory Power.*

When the variety of a carbo-hydrate under examination has to be decided, the determination of its optical activity is of primary importance. This property can also be very usefully employed in quantitatively estimating these bodies when the exact activity of the particular substances under consideration is known. It serves, too, as an important control to determinations made by other methods; indeed it is the only means we have of determining accurately the relative quantity of some of these bodies when occurring together, as for example, in mixtures of lævulose and dextrose. The specific rotatory power of an optically active body is simply the standard to which the activity is referred for the sake of comparison. Divested of all complication, it is the angle through which the plane of polarisation of a given ray is rotated, by passing through a layer 1000 mm. in length of a solution containing 10 grms. dry substance, or of known composition in 100 c.c. There are many instruments in use for measuring this angle. The one I employ is known as that of Soleil, made by Duboscq of Paris. The observations were taken in a tube 220 mm. in length, the neutral tint $[\alpha_j]$ being always worked with. On this point it is as well that no misunderstanding should exist, for I find that an inexact way of looking at these signs is finding its way into the journals, and if this be not noticed in time it will lead to much confusion. It would be well if observers, in giving the optical activity of a body, would state the angle they find for the specific rotatory power of cane sugar under the conditions of their work. As I have said elsewhere, I find the specific rotatory power of that body to be $[\alpha_j] = 73{\cdot}8^\circ$. I may state, too, how the powers in this investigation were determined. A solution was made by dissolving a weighed quantity of dry substance to a known volume of solution, or the quantity in solution was inferred from the specific gravity. The 220 mm. tube was then filled with the liquid, and an observation made. The number of divisions of the scale required for compensation were then converted into degrees by the equation

(i.) $100 : 24 = d : x$.

$d$ = the divisions observed, and

$x$ = the angle in degrees corresponding to them, 100 divisions being equal to 24°.

This is for the layer 220 mm. in length, but as 1000 mm. is the standard, another equation is necessary,

(ii.) $220 : 1000 = x : y$.

$y$ = the angular deviation for 1000 mm.

If the solution contained 10 grms. dry substance in 100 c.c., then $y$ = specific rotatory power; but if the solution contained $z$ grms. in the same quantity of liquid, then

(iii.) $z : 10 = y$ : specific rotatory power.

Equations (i) and (ii) can be united by the proportion

(iv.) $11 : 12 = d : y$.

Having thus detailed the modes of observation employed, I shall now proceed to give an account of the work itself.

## II. *Cold Malt-extract does not act on Ungelatinized Starch.*

The cold extract of 10 grms. malt was added to 10 grms. air-dried starch, containing 16·3 per cent. of water; at the end of 24 hours the starch was collected on a weighed filter. The filtrate was found to have the same specific gravity as the malt-extract employed, and the starch (well washed with cold water, then dried *in vacuo* for 36 to 40 hours, and afterwards at 110°) to have lost nothing in weight but the 16·3 per cent. of water of hydration which it originally contained. If the starch be heated to 110° before the greater portion of the water is expelled, by drying *in vacuo*, it becomes coloured, undergoing changes not yet examined, which prevent an exact determination of the moisture.

The experiment was repeated with dehydrated starch. On adding the cold malt-extract a considerable rise of temperature was observed. At first I thought this was due to the action of the extract which I found on examination had increased slightly in specific gravity; on drying the starch collected on a tarred filter, however, it proved to have lost nothing in weight. To what, then, was the rise of temperature and the slight increase in gravity of the extract to be attributed?

When cold water was added to dehydrated starch, the same evolution of heat was observed, this is due therefore to the chemical union of the dry starch with water to form a hydrate, and the slight increase in gravity of the extract to the concentration of the solution by the loss of this water.

III. *Malt-extract begins to dissolve Starch at the temperature of Gelatinization, or a few degrees lower.*

Starches from different sources do not gelatinize at the same temperature, nor do all the granules of a sample from the same source undergo this change at the same point. Thus I have found that on adding malt-extract to starch, and raising the temperature gradually, a certain portion is dissolved at one point, a further portion at a higher stage, and so on; the complete solution of pure potato starch being only effected at 62°—64°. The starch of maize, rice, and the small granule starches in general, require a temperature many degrees higher; in some cases I have found the transforming power of the extract destroyed before some of the granules gelatinized. Indeed, the complete solution of some starches cannot be effected; rarely, however, does the quantity remaining insoluble exceed 4 per cent. Maltose and dextrin in definite proportions are always produced if the temperature at which solution takes place be below 63°, and the malt-extract in no great excess.

IV. *Malt-extract dissolves Gelatinized Starch in the cold* (10°—20°) *almost completely if the gelatinization be perfect.*

5 grms. of starch were gelatinized in the usual way, the paste cooled to 16°, and 15 c.c. malt-extract added containing 0·436 grm. solid matter, calculated from sp. gr., and having an optical activity in 100 c.c. solution for a layer 1000 mm. in length = 1·64°, with a cupric oxide reducing power representing 0·124 grm. dextrose. On standing for a few hours, the insoluble portion, amounting to not more than 4 per cent., was filtered out, and the filtrate made up to 100 c.c. at 15·5°, so as to admit of the proper correction for the malt-extract. This solution did not colour iodine. Its specific gravity at 15·5° (all the specific gravities in these experiments were weighed at that temperature) was 1014·54 = 3·7766 grms. solid matter in the 100 c.c. The optical activity was found to be + 58·75°. 8·3546 grms. of the solution reduced 0·2858 grm. cupric oxide = 0·2858 × 0·4535 = 0·1296 grm. dextrose. Hence—

8·3546 : 101·45 (the weight of 100 c.c. solution) = 0·1296 : $x$.
$x$ = the cupric oxide expressed as dextrose, reduced by the solid matter in 100 c.c. solution = 1·5738 grm.

Of this 0·124 grm. is due to the malt-extract employed: therefore 1·5738 − 0·124 = 1·4498 grm. substance yielded by the starch. The total matter in 100 c.c. = 3·7766 grms.; of this the malt-extract furnishes 0·436, consequently 3·7766 − 0·436 = 3·3406 grms. derived

from the starch. The reduction of cupric oxide is shown above to be = 1·4498 grm. dextrose: hence—

$$3{\cdot}3406 : 1{\cdot}4498 = 100 : x.$$
$$x = \text{cupric oxide reducing power} = 43{\cdot}4, \text{ and}$$
$$43{\cdot}4 \div 0{\cdot}65 = 66{\cdot}7 \text{ the per cent. of maltose.}$$

This number can be arrived at in another way by multiplying the cupric oxide found by 0·4535 ÷ 0·65 = 0·6823 to find the maltose to which it corresponds, the remainder of the calculation being the same as before; but the reduction obtained for the malt-extract must be allowed for in powers of maltose instead of dextrose.

We have now to consider the use that can be made of the angular value.

3·7766 grms. solid matter in 100 c.c. = + 58·75°.
3·3406 grms. are from the starch:
the malt-extract in 100 c.c. = + 1·64°.

Hence 58·75° − 1·64° = 57·11°, the optical activity of the starch products. Then—

(iii.) 3·3406 : 10 = 57·11° : 171 , the specific rotatory power of these products. The same power calculated for a mixture containing 66·7 per cent. maltose, and 33·3 per cent. dextrin would be 171·3°, agreeing closely with the observation.

Or the proportion of maltose and dextrin can be calculated from the angle observed, 171°.

$x$ = maltose, $10 - x$ = dextrin. Then,
$15\,x + 214 - 21{\cdot}4\,x = 171°$.*

$x$ = 6·72 grms. maltose in 10 grms. mixture. 10 − 6·72 = 3·28 grms. dextrin, corresponding again with 6·67 and 3·33 from the reduction with cupric oxide.

The proportions of maltose and dextrin given in this experiment are those usually found if the solution be filtered and analysed within a few hours of adding the extract to the paste; if, however, the reaction be allowed to extend over a greater length of time, the maltose increases at the expense of the dextrin, more especially if the extract be in excess.

A little less than 4 grms. starch was treated in the way described in the last experiment, and 15 c.c. of malt extract of the same strength and composition added. At the end of 24 hours the insoluble portion was filtered out, and the filtrate made up to 100 c.c. at 15·5°. The specific gravity of this solution was found to be 1012·26 = 3·184 grms. solid matter, the optical activity observed = + 46·06°, and 9·9585 grms. of it gave 0·3445 grm. cupric oxide. These results calculated and the

* 1 grm. maltose in 100 c.c. solution = 15°; 1 grm. dextrin = 21·4°.

correction for the malt-extract made as before described, give the matter from the starch as composed of—

| | |
|---|---|
| Maltose..... | 82 per cent. |
| Dextrin..... | 18 „ |

with an observed specific rotatory power $[\alpha_j] = + 161{\cdot}2°$. The same calculated for a mixture of maltose and dextrin in the proportions found $= + 161{\cdot}6°$.

In decompositions of this kind I have found as much as 90 per cent. maltose, and between this and 67 per cent. a great variety of intermediate quantities have been observed, the maltose increasing with the duration of contact and the strength of the malt-extract.

(V.) *When Starch is dissolved by Malt-extract at any temperature below* 63°, *if the solution be immediately* (5 *to* 10 *minutes*) *cooled and filtered, the product invariably contains Maltose and Dextrin in proportions agreeing closely with* 67·85 *per cent. of the former, and* 32·15 *per cent. of the latter, the cupric oxide reducing power being* = 44·1, *and the specific rotatory power* $[\alpha_j] = 170{\cdot}6°$.

Innumerable decompositions have been made under the conditions of temperature mentioned, and I have found no particular precautions necessary to obtain a product of the percentage indicated. The malt-extract was heated to the point at which it was desired the reaction should take place, and added to the paste cooled to the same temperature; the whole was then placed on a water-bath at a like heat. When the paste had disappeared the solution was rapidly cooled and filtered, the filtrate giving no coloration with iodine; but if the solution be heated immediately to the boiling point before removing the insoluble residue (seldom amounting to 0·25 per cent. of the starch taken), the filtrate almost always gives a colour with the reagent. This colour is sometimes blue, sometimes reddish-brown, sometimes both, the brown hiding the blue; a drop or two of ammonia immediately discharges the former and leaves the latter. If the iodine test be not carefully applied, a small quantity of $\alpha$-dextrin is easily overlooked. The best way to apply it is as follows. Two clear glass cylinders, such as are employed in estimating ammonia by the Nessler method, are partially filled with water, placed on a sheet of white paper before a window, and a few drops of iodine solution added to each so as to obtain the same tint in both. If a little of a solution containing the least trace of $\alpha$-dextrin be added to either of these, a change in its colour will be immediately observable when contrasted with the other. I mention these facts, because much stress has been laid by other observers on the disappearance of the iodine reactions as

an indication of the completion of the transformation. Its value will be understood from what is here stated; and when I mention that a solution may give with iodine a deep blue coloration without showing any material change in the proportion of maltose, the value of the test will be better seen; 0·1 per cent. of soluble starch would give rise to the reaction. The solutions were all treated and analysed in the manner described under (IV); it is unnecessary, therefore, to go into the details of the observations and calculations. I must, however, give the results of a few decompositions made at different temperatures, and I select four, (*a*) made at 30°, (*b*) 40°, (*c*) 50°, and (*d*) 60°.

| | | Percentage of maltose. | Observed sp. rot. power. | Calculated sp. rot. power. |
|---|---|---|---|---|
| (*a*) | = | 68·1 | 169·7° | 170·4° |
| (*b*) | = | 67·4 | 170·7 | 170·8 |
| (*c*) | = | 66·7 | 169·9 | 171·4 |
| (*d*) | = | 68·3 | 170·8 | 170·2 |

These numbers agree closely with those given in Statement (V), and are a fair average of very many determinations. There is, therefore, under the conditions given, a definite reaction; the equation—

$$\text{(A.)}\ \underbrace{C_{18}H_{30}O_{15}}_{\text{Starch.}} + OH_2 = \underbrace{C_{12}H_{22}O_{11}}_{\text{Maltose.}} + \underbrace{C_6H_{10}O_5}_{\text{Dextrin.}}$$

requires

| | |
|---|---|
| Maltose ..... | 67·85 per cent. |
| Dextrin ..... | 32·15 ,, |

and sp. rot. power of mixture $[\alpha_j] = 170·6°$.

A comparison of these theoretical numbers with those found will leave no doubt as to the character of the reaction, and from the rapidity with which solution takes place, it cannot be questioned that it is a decomposition attended with hydration.

According to the equation, 100 parts of starch should yield 103·7 parts of the mixture, the increase being due to the fixation of the water molecule. I have estimated this increase in many experiments, and found it vary from 3·5 per cent. to 5 per cent. As an example of the method employed, I may describe one estimation.

5 grms. of starch were gelatinized and treated at 60° with the extract of 1 grm. of malt. The solution was completed at the end of three or four minutes, when it was cooled, and filtered through a tarred filter. The filtrate was made up to 100 c.c. at 15·5° with the washings. The insoluble portion and filter were dried first *in vacuo*, and then at 110°; the moisture in the starch was also estimated in this way; the amount of substance undissolved was found to be 0·076 grm. Dried in the same way 5 grms. of the starch employed

lost 0·815 grm. water; hence the starch dissolved was equal to 5 − (0·815 + 0·076) = 4·109 grms. The specific gravity of the solution (100 c.c.) was found to be 1017·4 = 4·5195 grms. substance. Of this, 0·2182 grm. was due to the malt-extract; consequently 4·3013 were derived from the 4·109 grms. of starch dissolved, which is in the proportion of 104·6 to 100. This solid matter was found to contain 67·69 per cent. maltose, and to have a sp. rot. power = + 171·3°. Many estimations made in this way gave as a rule between 3·5 and 5 per cent. for the increase. These numbers are certainly not far from the theoretical quantity; still they would seem to indicate that the values for the sp. grs. are 0·5 per cent. too high. As, however, they are well within the ordinary limits of error of manipulation, and as pure maltose and pure dextrin have given numbers on the mean of which the specific gravities are calculated, I am inclined to retain them.

If the malt-extract employed in these experiments be not in considerable excess, very little change takes place in the proportion of maltose and dextrin at first produced, even if the solution be retained for four or five hours at the temperature at which the decomposition was made.

An experiment in which the solid matter in the malt-extract employed was equal to 4 per cent. of the starch taken, the solution being kept five hours at 55°, gave—

Maltose = 68 per cent. from cupric oxide reducing power.
Sp. rot. power = 169·5°.

The sp. rot. power calculated for a mixture containing 68 per cent. maltose and 32 per cent. dextrin = 170·5°.

The same results were obtained by continuing the digestion eight hours, but if the malt-extract were in excess, or contained more acid than usual, on continuing the digestion after the solution had taken place, the maltose was found to increase at the expense of the dextrin, and to undergo a slight hydration itself. These changes are slow and gradual processes. The following are examples:—

A portion of starch was dissolved at 55° by cold malt-extract having a strongly acid reaction, and containing solid matter equal to 8 per cent. of the starch taken. The solution was maintained at the same temperature for eight hours. At the end of that time the solid matter dissolved was found to have a cupric oxide reducing power = 56, corresponding to 86·1 per cent. maltose, and a sp. rot. power = 154°. The same number calculated for a mixture containing 86·1 per cent. maltose and 13·9 per cent. dextrin is 158·89°, or 4·89° more than the observed angle.

In another experiment in which the malt-extract held about the

same relation to the starch, but was far less acid, I continued the digestion 18 hours. The cupric oxide reducing power was then found to be = 60, representing 92·3 per cent. maltose, and the sp. rot. power = 150°. The angle calculated for a mixture containing maltose = 92·3 per cent. and dextrin = 7·7 per cent., is 154·9°, or 4·9° more than the observed angle.

In the experiments where the digestion was continued for many hours, I found that the rotatory power calculated from the cupric oxide reducing power was invariably greater than that observed. This is due to the slow and gradual conversion of the maltose into dextrose (or, as I have reason to believe, two dextroses, having a united optical activity = + 67°) by the action of the acid of the malt-extract. The conversion of dextrin into maltose I am inclined to attribute to the active transforming agent of the extract, and that of maltose into the dextroses to the acid it contains; water alone does not seem to produce these changes. The difference between the observed sp. rot. power and the calculated one is due to the conversion of maltose.

10 grms. pure maltose were digested 10 hours with malt-extract containing 0·7 grm. solid matter. The cupric oxide reducing power was found to have increased to 73, and the sp. rot. power to have diminished to 131°. From these numbers the amount of dextrose produced and its sp. rot. power can be determined.

The dextrose from maltose has been proved to have a cupric oxide reducing power = 100.

$$\text{Let } x = \text{maltose}$$
$$\therefore 10 - x = \text{dextroses}$$
$$\text{then } x \times 0{\cdot}65 + 10 - x = 7{\cdot}3$$
$$0{\cdot}35\,x = 2{\cdot}7$$
$$x = 7{\cdot}71 \text{ maltose}$$
$$\text{and } 2{\cdot}29 \text{ dextroses.}$$

Then $131 - (7{\cdot}71 \times 15) = 15{\cdot}35°$, the activity of 2·29 grms. dextrose in 100 c.c.; hence $\frac{15{\cdot}35}{2{\cdot}29} = 6{\cdot}7$ the activity of 1 grm.; therefore sp. rot. power = 67°.

10 grms. of pure dextrin treated in the same manner for 10 hours gave a cupric oxide reducing power equal to 30 per cent. maltose. The optical activity was less than that of a mixture containing 30 per cent. maltose and 70 per cent. dextrin. This is due to the conversion of a small quantity of maltose into dextroses. I shall have more to say on this subject when I come to describe the action of sulphuric acid and other acids on maltose and dextrin.

It will be seen then from these experiments that at temperatures below 62°—63°, starch is split up into equivalent quantities of maltose

and dextrin by the action of malt-extract; and when the digestion is continued under certain conditions, dextrin yields maltose by gradual hydration. By the same process maltose is much more gradually converted into dextroses. If the solution be boiled, these changes do not take place on digestion.

VI. *When Starch is dissolved by Malt-extract at any temperature between* 64° *and* 68°—70°, *if the solution be immediately cooled and filtered the product invariably contains Maltose and Dextrin in proportions agreeing closely with* 34·54 *per cent. of the former and* 65·46 *per cent. of the latter, the cupric oxide reducing power being* = 22·4, *and the sp. rot. power* $[\alpha_j]$ = 191·8°.

Starch-paste at 66° was treated with malt-extract heated to the same temperature; at the end of four or five minutes, the paste having almost completely dissolved, the solution was cooled and filtered; the filtrate gave no reaction with iodine, while the insoluble portion, although it did not amount to 0·5 per cent. of the starch employed, gave a blue colour, and would, if heated to boiling while still in the liquid, impart to the filtrate the power of colouring iodine blue, reddish-brown or both.

The matter in solution derived from the starch, analysed according to the method already described, was found to have a cupric oxide reducing power = 22·4, representing 34·5 per cent. maltose, and a specific rotatory power = 192·9°.

I may give the numbers obtained in one experiment:—

Starch employed = 3·04 grms.
Malt-extract employed = 10 c.c., containing 0·2478 grm. solid matter.
Time required for solution = 4 minutes.
Temperature at which solution took place = 66°.
Quantity of filtered solution obtained = 100 c.c. at 15·5°.
Sp. gr. of ditto = 1010·63 = 2·761 grms. solid matter in the 100 c.c.
The optical activity of ditto = + 50·1°.
10·025 grms. solution gave 0·1405 cupric oxide.
10 c.c. malt-extract employed gave 0·1791 cupric oxide.
3·04 grms. of the starch employed lost on drying 0·5635 grm. water, and there remained 0·0096 grm. of it insoluble.
The malt-extract had an optical activity = + 16°: hence 10 c.c. of it diluted to 100 c.c. = + 1·6°.

When these numbers are calculated as described under (IV), we get for the matter dissolved from the starch—

Maltose ..... = 34·5 per cent.
Dextrin ..... = 65·5 ,,
Sp. rot. power $[\alpha_j]$ = + 192·9°.

The same power calculated for a mixture containing dextrin and maltose in the proportions found from the amount of cupric oxide reduced = + 191·9°.

101·9 parts of the mixture were obtained from 100 parts starch.

This experiment was repeated many times with varying quantities of starch from different sources (malt-starch, the starches of rice, maize, wheat, wheat-malt, &c.) and malt-extract; the results obtained on analyses of the products were never found to differ from those given by more than 1 or 2 per cent. of maltose either way, a corresponding variation of a few degrees similarly occurring in the specific rotatory power.

The equation—

$$(B.)\ \underbrace{\left.\begin{matrix}C_{18}H_{30}O_{15}\\ C_{18}H_{30}O_{15}\end{matrix}\right\}}_{\text{Starch.}} + OH_2 = \underbrace{C_{12}H_{22}O_{11}}_{\text{Maltose.}} + \underbrace{4C_6H_{10}O_5}_{\text{Dextrin.}}$$

requires—

Maltose ..... 34·54 per cent.
Dextrin ..... 65·46 ,,
Sp. rot. power of mixture $[\alpha_j]$ = 191·8°.
100 parts of starch to yield 101·8 parts mixture.

A comparison of these numbers with those found leaves no doubt but that equation (B) truly represents what takes place under the conditions.

In this case, as in the preceding one, if the malt-extract be not in excess, the relation of the maltose to the dextrin is not materially altered by three or four hours' digestion at the temperature of decomposition; but if, on the contrary, the extract be in excess or strongly acid, the dextrin yields maltose as before; while, if the digestion be continued for a sufficient time, the maltose is partially converted into dextrose. If the solution be boiled previous to digestion, the dextrin is not converted into maltose to any extent. If the unboiled solution be digested for a sufficient time with excess of malt-extract, the greater part of the dextrin may be made to yield maltose, and by varying the time and the quantity of extract, any proportions of dextrin and maltose may be obtained. I need not give the analyses which have led to these conclusions; sufficient has been already shown with regard to them under (V).

VII. *When Starch is dissolved by Malt-extract at temperatures from* 68°—70° *to the point at which the activity of the transforming agent is destroyed, if the solution be cooled and filtered at the end of five to ten minutes, the product contains Maltose and Dextrin in proportions agreeing closely with* 17·4 *per cent. of the former and* 82·6 *per cent. of the latter, the sp. rot. power of the mixture being* $[\alpha_j] = +$ 202·8°, *and cupric oxide reducing power* = 11·3.

These numbers are required by the equation—

$$(C.)\ \underbrace{\left.\begin{matrix} C_{18}H_{30}O_{15} \\ C_{18}H_{30}O_{15} \\ C_{18}H_{30}O_{15} \\ C_{18}H_{30}O_{15} \end{matrix}\right\}}_{\text{Starch.}} + OH_2 = \underbrace{C_{12}H_{22}O_{11}}_{\text{Maltose.}} + \underbrace{10C_6H_{10}O_5}_{\text{Dextrin.}}$$

By dissolving starch at temperatures between 69° and 76° with malt-extract heated to the same points, I have found products containing from 16·26 per cent. to 18·27 per cent. maltose, and having a specific rotatory power varying from 202° to 205°. These numbers are the extremes of many decompositions, and they agree sufficiently well with the theoretical ones.

I need not give details of calculations; all that is necessary to show how the determinations were made has been previously said.

The character of the dextrin obtained in this decomposition is the same as that produced according to equations (A) and (B); it is gradually converted into maltose by excess of malt-extract, but it can be digested four or five hours with a quantity necessary to dissolve the starch without undergoing any marked change. If the solution be carefully cooled and filtered, the filtrate is not coloured by iodine.

In the early stages of this investigation I was less or more inclined to look upon the conversion of starch into maltose by the action of diastase as a simple act of gradual hydration, soluble starch being formed first, then $\alpha$-dextrin, then $\beta$-dextrin, then maltose; and until I eliminated the conditions under which the molecular splitting-up, according to equations (A), (B), and (C), takes place, and found by direct experiment that dextrin was gradually converted into maltose, the evidence was strongly in favour of that conclusion. We have only to consider from what has been here described, how easy it is, with varying proportions of malt-extract and starch, and time and temperature, to obtain quantities of maltose varying from 16 to 92 per cent., and if these conditions were not clearly understood, how natural would be the conclusion that starch is converted into maltose by slow and gradual hydration.

I have not stated the proportion of the malt-extract to the starch

which I consider an excess, for as all malts do not contain the same amount of transforming agent, this can only be given approximately. I have found a cold extract of 1 grm. of one malt go as far as that of 3 grms. of another. It may, however, be stated that a quantity of extract containing solid matter equal to 5 per cent. of the starch taken, is in almost all cases sufficient for the reactions. By thoroughly working out the relative transforming power of different kinds of malt on the principle here indicated, there can be no doubt that results of considerable importance to the brewer and distiller will be obtained. At present I must be satisfied with simply drawing attention to the subject.

If the equations (A), (B), and (C) given above be examined, one cannot help being struck with the remarkable phenomena they describe. Is the starch molecule when broken up at 70°—76° twice as large as when it is broken up at 64°—68°, and is it in this latter case twice as large as when split up at all temperatures below 63°? Or are the results represented by the three equations due to some change brought about by heat in the character of the transforming agent? Or does malt-extract contain three distinct transforming bodies, one decomposing starch according to equation (A), its activity being destroyed at 64°, another, as in equation (B), destroyed at 68°—70°, whilst a third causes decomposition according to equation (C), becoming inactive at a point not yet determined? At present, I must not touch upon these questions, but must content myself with the account of a few experiments which seem to throw some light on the matter.

To about 4 grms. starch, gelatinized and cooled to 60°, 10 c.c. malt-extract containing 0·2883 grms. solid matter, heated to 67° for a few minutes and then cooled to 60°, was added. Solution immediately followed, and at the end of about five minutes the liquid was cooled and filtered. The filtrate, which gave no coloration with iodine, was found to contain, on analysis by the method already indicated, solid matter from the starch of which 34·8 per cent. was maltose and 65·2 per cent. dextrin, its sp. rot. power being + 190·8°.

The same results were obtained several times, various proportions of malt-extract and starch being employed. The numbers agree with those required by the decomposition according to equation (B).

By heating malt-extract to 75°, cooling to 68°, and dissolving starch-paste with it at 68°, numbers required by the decomposition according to equation (C) were obtained. Hence it would appear that the various decompositions are not due to any difference in the size of the starch-molecule, but to some change brought about by heat in the character of the decomposing agent or agents.

If the phenomena which I have described in this paper be considered, and the results compared with those of previous workers on

the subject, it will not be difficult to see whence their very contradictory statements have sprung, and how easily they may all be accounted for. The decomposition of starch into maltose and dextrin is *molecular*, and does not take place according to one equation, but to three; the conversion of dextrin into maltose is a slow and gradual act of *hydration*.

I have to thank my brother James for much valuable assistance in carrying out this work.

## VIII.—*On the Gases enclosed in Cannel Coals and Jet.*

By J. W. Thomas.

The analyses of the gases enclosed in anthracite, bituminous, and steam coals, were given in a former paper (*Chem. Soc. J.* [2], xiii, 793), and reference made to the work which had been previously done in this direction. The gases enclosed in cannel,—another important class of coal used for the manufacture of coal-gas, &c.,—have not, as far as I am aware, been determined.

The method used for obtaining the enclosed gases was similar to that described in the paper referred to, with the exception that Florence flasks, having their necks drawn out and bent over, were substituted for glass tubes when Scotch cannel was employed,—a large quantity of coal being required to furnish the necessary volume of gas. These coals were broken in a mortar and passed through a sieve having 9 meshes to the inch, and the dust was removed by a sieve having 64 meshes to the inch.

The following table shows from whence the cannel coals and jet were obtained :—

| No of Sample. | Description. | District. |
|---|---|---|
| No. 1 | Wigan cannel ⅔ seam, 350 yards deep. | Wigan Arley Mine, Lancashire coal field. |
| 2 | Wigan cannel ⅔ seam, 600 yards deep. | Lancashire coal field. |
| 3 | Scotch cannel (Heywood cannel (Wilsontown). | Lanark. |
| 4 | Scotch cannel (Lesmahago). | |
| 5 | Whitehill cannel shale, Lasswade. | Edinburgh. |
| 6 | Whitby jet (finest quality for ornaments). | Whitby. |

Cannel coals are usually very hard and close-grained, fracturing conchoïdal, without crumbling, and when placed in a vacuum do not evolve any appreciable quantity of gas. No. 1 was somewhat porous, and resembled, in appearance, the hardest steam coals of the South Wales Basin.

The following are the results I obtained :—

SAMPLE No. 1.—*Wigan Cannel from Wigan Arley Mine.*

100 grms. of coal evolved 421·3 c.c. of gas at 100°.

The last portion of air exhausted in forming a vacuum contained 20·54 per cent. of oxygen.

*Analysis of the Gas Evolved at* 100°.

| Observed pressure of gas (dry). | Temperature. | Corrected vol. at 11°. | Progress. |
|---|---|---|---|
| 91·7 mm. | 11·3 | 91·60 | Volume employed. |
| 85·7 mm. | 11·0 | 85·70 | Volume after absorption of $CO_2$. |
| 85·7 mm. | 11·0 | 85·70 | Volume after absorption of O. |
| 342·5 mm. | 11·0 | 342·50 | Volume after adding O. |
| 183·6 mm. | 11·1 | 183·53 | Volume after explosion. |
| 101·1 mm. | 11·5 | 100·92 | Volume after absorption of $CO_2$. |
| 347·9 mm. | 11·9 | 346·76 | Volume after adding H. |
| 66·5 mm. | 11·9 | 66·30 | Volume after explosion. |

| | Composition in 100 parts. |
|---|---|
| Carbonic anhydride | 6·44 |
| Marsh-gas | 80·69 |
| Hydride of ethyl | 4·75 |
| Nitrogen | 8·12 |
| | 100·00 |

SAMPLE No. 2.—*Wigan Cannel.*

100 grms. of coal evolved 350·6 c.c. of gas at 100°.

The last portion of air exhausted in forming a vacuum contained 20·77 per cent. of oxygen.

*Analysis of the Gas Evolved at* 100°.

| Observed pressure of gas (dry). | Temperature. | Corrected vol. at 11·6°. | Progress. |
|---|---|---|---|
| 127·0 mm. | 10·7 | 127·42 | Volume employed. |
| 115·6 mm. | 11·0 | 115·85 | Volume after absorption of $CO_2$. |
| 115·7 mm. | 11·2 | 115·90 | Volume after absorption of O. |
| 446·5 mm. | 11·6 | 446·50 | Volume after adding O. |
| 223·5 mm. | 11·8 | 223·34 | Volume after explosion. |
| 105·4 mm. | 12·4 | 105·10 | Volume after absorption of $CO_2$. |
| 7·6 mm. | 11·6 | 7·60 | Volume after absorption of O. |

| | Composition in 100 parts. |
|---|---|
| Carbonic anhydride | 9·05 |
| Marsh-gas | 77·19 |
| Hydride of ethyl | 7·80 |
| Nitrogen | 5·96 |
| | 100·00 |

The tube containing the coal was heated for two days until apparently exhausted, the last portion of gas brought over was of the following composition:—

*Analysis of last portion Evolved at* 100° C.

| Observed pressure of gas (dry). | Temperature. | Corrected vol. at 12·6°. | Progress. |
|---|---|---|---|
| 118·4 mm. | 12·6 | 118·40 | Volume employed. |
| 113·7 mm. | 12·6 | 113·70 | Volume after absorption of $CO_2$. |
| 433·0 mm. | 13·0 | 432·37 | Volume after adding O. |
| 197·6 mm. | 13·0 | 197·30 | Volume after explosion. |
| 66·8 mm. | 12·6 | 66·80 | Volume after absorption of $CO_2$. |
| 304·3 mm. | 12·6 | 304·30 | Volume after adding H. |
| 110·9 mm. | 12·6 | 110·90 | Volume after explosion. |

| | Composition in 100 parts. |
|---|---|
| Carbonic anhydride | 3·97 |
| Marsh-gas | 79·58 |
| Hydride of ethyl | 15·32 |
| Nitrogen | 1·13 |
| | 100·00 |

The first portion of sample No. 2 gave off gas readily, about twice its volume being evolved in six hours. On the second day it was again heated for 10 hours—some of the higher hydrocarbons of the paraffin series were condensed in the connecting-tube of the Sprengel, and also brought over by the pump. On the third morning, a white crystalline substance was formed in the connecting-tube, which, together with the tubes in which the gas was collected, emitted the odour of the oils obtained from petroleum distilled at 100°. I was unable to obtain satisfactory results, owing to the presence of so much oily matters brought over by the Sprengel pump. A second portion of the coal was taken and connected with the Sprengel in the usual manner. The branch tube holding the water-joint was made of extra length, and of such a form as to admit of its being surrounded with freezing mixture. The gas brought over was thus obtained more free from vapour of the higher hydrocarbons.

This coal was again heated to 200°, when a further quantity of gas was evolved equal to 276·2 c.c. per 100 grms. of coal. In spite of the cooling effect of the freezing mixture, some oily matters and vapour were brought over by the pump, and the results of the analysis were not sufficiently concordant to enable one to calculate the percentage of the hydrocarbons present. It was interesting, however, to observe the deposition of oily matters in the neck of the flask in which the coal was placed, as well as along a considerable length of the connecting-tube. This coal appears to hold in a condensed form the whole of the paraffins from $C_4H_{10}$ upwards, together with the gases $CO_2$, N, $CH_4$, $C_2H_6$, and probably $C_3H_8$.

A portion of this coal was maintained for eight hours under a partial vacuum at 50°, and the gas evolved smelt strongly like crude petroleum, and the surface of the water (from the coal) in the connecting-tube (which was immersed in freezing mixture) was covered with oily matter, which disappeared shortly after the apparatus was disconnected.

SAMPLE No. 3.—*Scotch Cannel, Haywood Colliery, Wilsontown.*

100 grms. of coal evolved 16·8 c.c. at 100°.

The last portion of air exhausted in forming a vacuum contained 20·86 per cent. of oxygen.

*Analysis of the Gas Evolved at* 100°.

| Observed pressure of gas (dry). | Temperature. | Corrected vol. at 15·0°. | Progress. |
|---|---|---|---|
| 134·4 mm. | 13·4 | 135·20 | Volume employed. |
| 62·0 mm. | 13·8 | 62·27 | Volume after absorption of $CO_2$. |
| 62·1 mm. | 13·8 | 62·37 | Volume after absorption of O. |
| 244·0 mm. | 15·0 | 244·00 | Volume after adding O. |
| 337·8 mm. | 15·0 | 337·80 | Volume after adding H. |
| 195·3 mm. | 14·0 | 196·00 | Volume after explosion. |
| 61·8 mm. | 14·2 | 61·98 | Volume after absorption of O. |

| | Composition in 100 parts. |
|---|---|
| Carbonic anhydride ..... | 53·94 |
| Nitrogen ..... | 46·06 |
| Traces of Hydrocarbons ..... | |
| | 100·00 |

SAMPLE No. 4.—*Lesmahago Cannel.*

100 grms. of coal evolved 55·7 c.c. of gas at 100°.

The last portion of gas exhausted in forming a vacuum contained 20·99 per cent. of oxygen.

*Analysis of the Gas Evolved at* 100°.

| Observed pressure of gas (dry). | Temperature. | Corrected vol. at 13°. | Progress. |
|---|---|---|---|
| 436·2 mm. | 13·0 | 436·2 | Volume employed. |
| 67·4 mm. | 13·0 | 67·4 | Volume after absorption of $CO_2$. |
| 67·3 mm. | 13·0 | 67·3 | Volume after absorption of O. |
| 67·2 mm. | 13·0 | 67·2 | Volume after absorption with ammonio-cuprous chloride. |
| 66·0 mm. | 14·0 | 65·75 | Volume after absorption with fuming sulphuric acid. |
| 205·3 mm. | 12·2 | 205·90 | Volume after adding oxygen. |

| Observed pressure of gas (dry). | Temperature. | Corrected vol. at 13°. | Progress. |
|---|---|---|---|
| 319·2 mm. | 12·6 | 319·66 | Volume after adding H. |
| 141·4 mm. | 12·8 | 141·50 | Volume after explosion. |
| 134·8 mm. | 13·0 | 134·80 | Volume after absorption of $CO_2$. |
| 322·0 mm. | 13·0 | 322·0 | Volume after adding H. |
| 107·4 mm. | 13·0 | 107·4 | Volume after explosion. |

| | Composition in 100 parts. |
|---|---|
| Carbonic anhydride | 84·55 |
| Nitrogen | 14·54 |
| Gases and vapour of the $C_nH_{2n+2}$ series agreeing with $C_3H_8$ | 0·91 |
| | 100·00 |

SAMPLE NO. 5.—*Cannel Shale, Lasswade, Edinburgh.*

100 grms. of the shale evolved 15·7 c.c. of gas.

The last portion of air exhausted in forming a vacuum contained 20·85 per cent. of oxygen.

*Analysis of the Gas Evolved at* 100°.

The absence of oxygen was proved by previous analyses.

| Observed pressure of gas (dry). | Temperature. | Corrected vol. at 15°. | Progress. |
|---|---|---|---|
| 312·9 mm. | 14·9 | 313·0 | Volume employed. |
| 97·8 mm. | 15·0 | 97·8 | Volume after absorption of $CO_2$. |
| 256·8 mm. | 14·6 | 257·17 | Volume after adding O. |
| 407·6 mm. | 15·0 | 407·60 | Volume after adding H. |
| 163·4 mm. | 15·0 | 163·40 | Volume after explosion. |
| 146·3 mm. | 15·2 | 146·20 | Volume after absorption of $CO_2$. |
| 389·4 mm. | 15·6 | 388·55 | Volume after adding H. |
| 218·9 mm. | 15·8 | 218·26 | Volume after explosion. |

| | Composition in 100 parts. |
|---|---|
| Carbonic anhydride | 68·75 |
| Gases of the $C_nH_{2n+2}$ series agreeing with $C_2H_6, C_3H_8$ | 2·67 |
| Nitrogen | 28·58 |
| | 100·00 |

SAMPLE No. 6.—*Whitby Jet (finest quality).*

100 grms. of jet evolved 30·2 c.c. of gas at 100°.

*Analysis of the Gas Evolved at* 100°.

| Observed pressure of gas (dry). | Temperature. | Corrected vol. at 13°. | Progress. |
|---|---|---|---|
| 55·2 mm. | 12·8 | 55·24 | Volume employed. |
| 49·2 mm. | 13·0 | 49·2 | Volume after absorption of $CO_2$. |
| 454·5 mm. | 12·8 | 454·83 | Volume after adding O. |
| 282·6 mm. | 13·0 | 282·6 | Volume after explosion. |
| 88·6 mm. | 13·0 | 88·6 | Volume after absorption of $CO_2$. |
| 387·4 mm. | 13·0 | 387·4 | Volume after adding H. |
| 125·2 mm. | 13·0 | 125·2 | Volume after explosion. |

| | Composition in 100 parts. |
|---|---|
| Carbonic anhydride ..... | 10·93 |
| Quartane or ethyl ..... | 86·90 |
| Nitrogen ..... | 2·17 |
| | 100·00 |

The contraction of volume after explosion, carbonic acid absorbed, and oxygen consumed when compared with the volume (sample 6), correspond nearly with $C_4H_{10}$, including probably a little vapour of other hydrocarbons higher in the series. Absolute alcohol absorbs more than three-fourths of the entire volume of gas withdrawn from jet, and gives it up again on the addition of water.

The following table gives the quantity of gases evolved as well as their composition:—

*Composition of Gases.*

| No. of Sample. | Gas evolved by 100 grms. of coal at 100° under a vacuum. | Carbonic anhydride. | Marsh-gas. | Hydride of ethyl. | Quartane or ethyl. | Nitrogen. |
|---|---|---|---|---|---|---|
| 1 | 421·3 c.c. | 6·44 | 80·69 | 4·75 | — | 8·12 |
| 2 | 350·6 c.c. | 9·05 | 77·80 | 7·80 | — | 5·96 |
| 3 | 16·8 c.c. | 53·94 | — | — | — | 46·06 |
| 4 | 55·7 c.c. | 84·55 | — | — | $\left\{ \begin{matrix} C_3H_8 \\ 0·91 \end{matrix} \right\}$ | 14·54 |
| 5 | 55·7 c.c. | 68·75 | — | 2·67 | — | 28·58 |
| 6 | 30·2 c.c. | 10·93 | — | — | 86·90 | 2·17 |

The coals examined by Meyer from the Newcastle and Durham coal-fields (abstract of paper, published in the *Journal für praktische Chemie* [2], v, 144—183; 407—427, and vi, 389—416 will be found in the *Chem. Soc. J.* [2], x, 798 and 801, and xi, 483), did not contain any hydrocarbon other than marsh-gas. The bituminous, anthracite, and steam coals, already referred to at the commencement of this paper, also contained only $CO_2$, $CH_4$, O and N as occluded gas.

It will be seen, however, that the cannel coals differ considerably from those mentioned, inasmuch as they enclose hydride of ethyl, and most probably $C_3H_8$, and all the paraffin series. I am unable to determine the presence or absence of $C_3H_8$ in a mixture containing $CH_4$ and $C_2H_6$, as

$$C_3H_8 + CH_4 = 2C_2H_6.$$

I have, therefore, calculated the volume of explosive gas as $CH_4$ and $C_2H_6$.

The whole of the cannel coals and jet contain the gases of the paraffin series and oily matters, which appear to belong to the same. Wigan cannels, with regard to the gases which they hold enclosed, occupy a position intermediate with steam and Scotch cannel; and Scotch cannel occupies a position intermediate with bituminous house coals and Wigan cannel. Thus, in the Wigan cannels, there is a large volume of gas, consisting for the most part of marsh-gas, with a low percentage of carbonic acid and nitrogen, and, *in these respects*, closely allied to the steam coals. The Scotch cannels, on the other hand, contain but little gas, which consists almost entirely of carbonic anhydride and nitrogen, similar to the bituminous class of house coals. Scotch cannel contains a small quantity of the higher hydrocarbon gases. Owing to the high percentage of carbonic anhydride present, it became possible to employ a large and concentrated volume for the determination of the combustible gases.

In the analysis of sample 4, the respective volumes of the contraction after explosion, carbonic anhydride formed, and oxygen consumed, when compared with the volume, agree nearly with hydride of propyl; it is possible, therefore, that $CH_4$, $C_2H_6$, $C_4H_{10}$ may be present also. In sample No. 5, $C_2H_6$ and $C_3H_8$ agree nearly with the respective volumes above mentioned.

The gases from all the cannel coals have been treated with fuming sulphuric acid and ammonio-cuprous chloride. Some of them showed indications of $C_nH_{2n}$ gases, but it is probable that the loss in volume was due to the absorption of the vapour of the higher hydrocarbons, because, when the whole volume of combustible gas was exploded, the $CO_2$ formed, O consumed, and contraction due to explosion, did not agree with the calculated volume.

Negative results were obtained with ammonio-cuprous chloride, showing the absence of carbonic oxide.

Absolute alcohol absorbed more or less gas in all instances, but the total volume of combustible gas was insufficient to obtain decided results with the Scotch cannels. The gases obtained from sample No. 5, after absorption with absolute alcohol, and exploding with oxygen by the aid of hydrogen, yielded only 1 per cent. of combustible gas, and the hydride of ethyl in cannel No. 2 was considerably lessened after absorption with alcohol.

Jet differs from the harder cannels by occluding only a small percentage of $CO_2$ and N, and also by containing a large percentage of $C_nH_{2n+2}$ gas. The tube in which the gases were brought over by the pump contained one- or two-tenths of a c.c. of oily matter emitting the odour of paraffin.

It is necessary when working with any coal, or carbonaceous material whatever, for the purpose of obtaining its enclosed gases, to first ascertain by experiment the volume which is evolved at the required temperature In this manner, a portion of the substance can be taken which shall yield the quantity of gas necessary for analysis, and shall not be too large to be collected in one tube; and the coal should be exhausted before using any of the gas for analysis, unless it be required to ascertain the deportment of the gases under a vacuum.

In conclusion, I would express my thanks to those gentlemen who favoured me with the coals and jet.

## IX.—*Phenomena accompanying the Electrolysis of Water with Oxidisable Electrodes.*

By Professor GLADSTONE, F.R.S., and ALFRED TRIBE, F.C.S.

IN a paper read at the meeting of the British Association in 1872, we pointed out that "the electrolysis of water is more easily effected between poles made of a metal that has a considerable affinity for oxygen than between poles that have little affinity." It was also stated that "when zinc poles were used, there was found to be more than double the action that there was when platinum poles of the same size and at the same distance were employed," and that the order of efficiency seemed to be platinum, tin, silver, copper, iron, lead, zinc, magnesium.

In performing these experiments, we found a wearing away of the

positive electrode, a formation of singular clouds and films in the liquid, and a growth of threads, fringes, or arborescent crystals of metal on the negative electrode. In the case of silver, when a thread of the metal touches the glass, it sometimes spreads over the surface as a thin translucent film, in which, however, a crystalline structure is easily discernible, but which is so thin that it appears green or purple by transmitted light.

Some of these phenomena were observed by Davy, and even in the original electrolysis of water by Nicholson and Carlisle, who employed, in the first instance, brass wires for the passage of the electricity; but no explanation is given by these early observers.

The explanation, however, is not far to seek.

In the case of the more active metals, the oxygen, of course, is not given off at the positive electrode as gas, but it combines with the metal to form an oxide, or rather hydrate, and as all the hydrates are probably more or less soluble in water, there is soon formed a dilute solution of the metallic compound in the space between the electrodes. This probably offers less resistance to the voltaic current than the water itself, and is successively decomposed, the final result being the deposit of metal on the negative electrode.

This corrosion of the positive electrode is, perhaps, assisted by another circumstance. We know, from the experiments of Davy, that when carefully distilled water which has been exposed to the air, is decomposed by a powerful battery, a small quantity of nitric acid is formed at the positive pole from the dissolved nitrogen. This, of course, might be expected to facilitate the solution of the metal. We did not employ powerful batteries, but single cells of Daniell or Grove, and we sought for this nitric acid by the extremely delicate carbolic acid test, and for nitrous acid by the iodide of potassium and starch test. Sometimes a trace was detected, at other times none. That the presence of a nitrate is not essential to the production of the phenomenon was proved, in the case of silver, by taking a solution of pure hydrate of silver in the purest distilled water, and electrolysing it between platinum electrodes, when the usual beautiful arborescent crystals of metal were obtained.

A series of comparative experiments were made with electrodes consisting of narrow plates of zinc, lead, iron, copper, silver, and platinum, and with the purest water collected direct from the pipe of the still. One cell of Grove was employed for each pair of electrodes; the arrangements were made strictly comparable, the only difference consisting in the nature of the metal, and the results were observed at the termination of 3 minutes, 15 minutes, 1 hour, 4 hours, and 22 hours.

In the case of zinc, the positive electrode was slightly oxidised in

3 minutes, and afterwards was distinctly eaten away at the lower part. Bubbles of gas formed almost immediately, escaping from the inner side of the negative electrode; accompanied in 15 minutes with a slight cloudiness of the neighbouring liquid; and in an hour with the formation of a white substance adhering to the inner side of the plate, and a little black deposit fringing the lower part. This formation of oxide and metallic zinc increased, and at the end of 22 hours 1·5 c.c. of gas had been collected. The black deposit examined by the microscope was found to be crystallised zinc, and no trace of a nitrogen-compound could be detected in the solution.

In the case of lead, the positive electrode showed signs of slight oxidation, and the negative electrode a few small bubbles, in 15 minutes; a slight cloudiness was then beginning to form, which afterwards increased; some oxide was found adhering in an hour; and afterwards grey metallic lead, which at the end of 22 hours was found to have stretched across to the positive electrode, forming a metallic connexion which was so much heated by the passage of the voltaic current that the liquid became warm. About 0·5 c.c. of gas was collected.

In the case of iron, the oxidation of the positive electrode was observed in 15 minutes, and at the end of the experiment it was almost black. On the negative electrode, a minute bubble or two and a faint cloud were observed in 3 minutes' time. A yellowish-red oxide soon made its appearance, and afterwards a whitish-green oxide, which turned red on exposure to the air. There was also a dark deposit of iron from which gas was evolved for some minutes after disconnecting the battery. This was doubtless due to the fact that finely divided iron decomposes water of itself. About 2·5 c.c. of gas were collected in the 22 hours.

In the case of copper, no tarnishing of the positive electrode was observed till the 4-hour period; but in 15 minutes, though there was no gas, there was a slight cloudiness in the liquid near the inner side of the negative electrode; in 1 hour, fragments of green hydrate adhered to it, and there was a growth of black from the lower edges. In 4 hours it was covered with black powder, while the growth at the edges increased. In 22 hours the gas produced was scarcely to be measured, but the black and red crystallised copper was considerable in quantity.

In the case of silver, a slight tarnishing of the positive electrode appeared in one hour, no gas formed at the negative electrode, but there was a cloudiness in 15 minutes, and a fringe of metal in one hour, which gradually extended till it joined the positive electrode, while the liquid, in consequence, became warm. The silver spread over the glass with its usual beautiful appearance.

In the case of platinum there was no visible result at all.

At the conclusion of the experiment, the water in which the iron electrodes had been immersed gave a faint blue tinge with ferrocyanide of potassium; the water, with the lead and copper electrodes, gave a faint, and that with the silver electrodes, a very distinct blackening with hydrosulphuric acid.

The comparative solubility of these metallic hydrates in water has, no doubt, great effect upon the ultimate result, though the different electromotive force, or affinity for oxygen, of the various metals must be looked upon as causing the initial difference.

# ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

## General and Physical Chemistry.

### Production of Spectra by the Oxyhydrogen Flame.

By T. H. MARVIN (Phil. Mag. [5], i, 67).

To produce bright line spectra without a continuous spectrum, the author has employed a method in which he uses artificially prepared cylinders of the substance upon which he is going to work. This cylinder is slipped upon a double oxyhydrogen jet, so that the flame may play upon opposite sides of the inner surface of the hollow cylinder. This throws a flame directly upwards, from which the spectrum may be obtained; and the incandescent points being within the cylinder, no continuous spectrum is possible. The author has obtained good results with cylinders of calcium and strontium. When an easily fusible oxide is to be examined, the cylinder must be mixed with some infusible substance, like alumina, to prevent fusion. The author has, to a certain extent, been successful in photographing the spectra obtained.

J. M. T.

### Absorption-spectra of Metals Volatilized by the Oxyhydrogen Flame.

By J. NORMAN LOCKYER and W. CHANDLER ROBERTS (Phil. Mag. [5], i, 234—239).

RECENT researches on the absorption-spectra of metals published by Roscoe, Schuster, and the authors, have established the following.

1. In addition to the well-known line spectra, channelled-space spectra are produced by the vapours of certain metals; and

2. Such spectra are produced by vapours competent to give at other times not only line-spectra, but continuous spectra in the blue or blue and red.

As the temperature at which the former researches were conducted did not exceed bright redness, the authors considered it desirable to extend the observations to less fusible metals, as well as to ascertain whether the spectra of these volatilized at lower temperatures were modified by a greater degree of heat.

The blowpipe used is that invented by Deville and Debray, and the lime-still employed by Stas in the distillation of silver with the blowpipe has been modified by the authors so as to admit of the metallic vapour being conducted into a lime-tunnel heated to whiteness, placed in such a position that a beam of light could readily traverse it. (A diagram with full description of the arrangement accompanies the paper.) An electric lamp from a 30-cell Bunsen battery is placed opposite one end of the tube, and a spectroscope opposite the other.

This last instrument was made by Desaga of Heidelberg, and its single prism, the angle of which was 60°, was capable of distinctly separating the D lines, at the same time enabling the operator to see the whole spectrum in a single field of vision. The magnifying power of the telescope was 7·5 linear. The lime-block with its fittings was placed in a charcoal furnace, by means of which the whole might be raised to a high temperature. As soon as the whole was at bright redness, the metal to be examined was placed in a small cavity in the lime support and the oxyhydrogen flame allowed to play on its surface, care being taken to have an excess of hydrogen. As the glass plates rapidly became coated by the condensation of the metallic vapours, an arrangement was introduced by which they could be easily replaced. To assure themselves that no oxides were present to destroy the results, the authors tested the lime-tube at the end of each experiment, when an excess of hydrogen was invariably found. The metals, with few exceptions, were melted in hydrogen and kept till required for experiment in sealed glass tubes. The effect of oxides and of the metallic rain due to condensation, was to produce a general absorption obviously different from the special effects of absorption. The authors give in detail the results of their experiments with each individual metal; these, however, are too long for abstraction. It appears, however, to the authors that the results obtained at the temperature of the oxyhydrogen flame support conclusions drawn from the results at lower temperatures. First, in passing from the liquid to the most perfect gas, vapours are composed of molecules of different orders of complexity; and, secondly, this complexity is diminished by the dissociating action of heat, each molecular simplification being marked by a distinctive spectrum. There is also an intimate connection between the facility with which the final stage is reached, the group to which the element belongs, and the space it occupies in the solar atmosphere.

J. M. T.

## On Neutralisation.

By Julius Thomsen (J. pr. Chem. [2], xiii, 241—270).

The results of the paper are summed up as follows:—While the heats of neutralisation of the alkalis and alkaline earths show great dissimilarity when these bodies are dissolved as anhydrides or as hydrates in acids, all discrepancies vanish if the heats of neutralisation of aqueous solutions are taken, and if the compounds formed also remain in a state of solution. In this case the evolution of heat on neutralisation of two equivalents of base is for hydrochloric acid 27,500 units, and for sulphuric acid 31,300 units, and these values are the true heats of neutralisation of the bases in question.

The compound bases allied to potassium hydrate—such as tetramethylammonium hydrate, triethylsulfin hydrate, platodiamine hydrate—possess the same heat of neutralisation. Ammonia, on the contrary, possesses a smaller heat of neutralisation than the alkalis—for sulphuric acid 28,150 units, and for hydrochloric acid 24,540 units. This value for ammonia is not altered by introducing alcohol-radicles

of the series $C_nH_{2n+1}$ into the molecule in place of hydrogen, the numbers becoming, for instance in the case of triethylamine, 28,340 and 25,040. The amines of the aromatic series, however, have a considerably smaller heat of neutralisation than ammonia, amounting, in the case of aniline and toluidine (for two molecules) for hydrochloric acid, to only 15—16,000 units. The reason is that the negative radicle $C_6H_5$, lessens the basic power of the ammonia.

Hydroxylamine also shows the influence of the substitution of a negative radicle, HO, in place of the hydrogen of ammonia, for the heat of neutralisation of hydroxylamine for hydrochloric acid is 18,500 units.

The organic bases which contain oxygen exhibit a similar phenomenon—methylquinine hydrate, for instance, has a heat of neutralisation of about 20,000 units for hydrochloric acid, that of tetramethylammonium hydrate being 27,500 units. And the difference becomes much greater if the oxygenised radicles are true acid radicles, as in the amides; the heat of neutralisation of urea, in which the basic character has almost disappeared, is 130 units per molecule. The bases which are soluble in water may therefore be divided into two groups:—

(1.) The group of hydrates, represented by potassium hydrate.

(2.) The group of anhydrides, represented by ammonia.

The typical heat of neutralisation of the first group is for one molecule of normal sulphate 31,300 units, that of the second 28,200 units at about 18°.

To the first group belong the alkalis, including thallium hydrate, the alkaline earths, the ammonium-bases of the alcohol-radicles of the fatty series, triethylsulfin hydrate, platodiamine hydrate, and probably many others whose radicle contains no negative particle.

To the second group belong ammonia and the substituted ammonias of the fatty alcohol radicles, and probably also other radicles possessing a character analogous to hydrogen.

If oxygenised or other negative radicles enter into the molecule of the base, the typical heat of neutralisation is lessened. This is the case with methylquinine hydrate, and probably with other quaternary bases containing oxygen: also with hydroxylamine, triethylstibine oxide, the aromatic amines and amides: in the latter the typical heat of neutralisation almost entirely disappears simultaneously with their basic character.

In the case of bases insoluble in water, only the apparent heat of neutralisation can be measured—it is the sum of the true heat and the heat of solution of the base.

Analogy leads to the conclusion, that for bases of the magnesia series, $RO_2H_2$, where R is replaceable by Mg, Mn, Fe, Ni, Co, Zn, and Cu, the true heat of neutralisation is similar to that of the alkaline earths, and that the heat of solution of these bases is—

| | | | |
|---|---|---|---|
| For Mg = | 0 units. | For Fe = | − 6300 units. |
| Mn = | − 4800 ,, | Zn = | − 7800 ,, |
| Ni = | − 5100 ,, | Cu = | −12800 ,, |
| Co = | − 6600 ,, | | |

Whilst the true heat of neutralisation of hydrochloric, hydrobromic, and hydriodic acids for the alkalis, the alkaline earths, the magnesia bases, the ammonias, &c., is found to be constant for each group, the apparent heat of neutralisation is very different for the three acids if the base forms an insoluble haloïd compound: it then becomes least for chlorine-, greatest for iodine-compounds: this is the case on neutralisation of these acids by PbO, $Tl_2O$, $Ag_2O$, $Hg_2O$, $Cu_2O$, and $Au_2O$, oxides which all possess only a slight affinity for water.

Investigations on the heat of solution of the haloïd compounds of lead and thallium show that the difference in the apparent heats of neutralisation of the three hydrogen-acids, for these two metals at any rate, arises from the inequality of the heats of solution of the haloïd compounds; the values found were—

$$(TlCl,Aq) = -10100 \text{ heat-units.}$$
$$(PbCl_2,Aq) = -\ 6800 \quad ,,$$
$$(PbBr_2,Aq) = -10040 \quad ,,$$

The apparent heat of neutralisation is the difference between the true one and the heat of solution of the compound formed: if, therefore, the heat of solution is added on to the apparent heat of neutralisation, the true heat of neutralisation is obtained, *i.e.*, that which would be observed if the solutions were so diluted that no precipitate formed. In this way it appears that the true heat of neutralisation of hydrochloric and hydrobromic acids by lead oxide is the same, and that the true heat of neutralisation of thallium also for the hydrogen acids is the same as that of the alkalis. By reasoning in this way it is possible to estimate, at all events approximately, the heat of solution of insoluble compounds, such as—

| | | | | | |
|---|---|---|---|---|---|
| TlCl | −10100 heat units. | $PbCl_2$ | − 6800 | AgCl | −15850 |
| TlBr | −13750 ,, | $PbBr_2$ | −10040 | AgBr | −20100 |
| TlI | −17850 ,, | $PbI_2$ | −16440 | AgI | −26420 |

Investigations of a similar kind gave for the heat of solution of the insoluble sulphates—

$$\left.\begin{array}{ll} BaSO_4 & -5600 \\ SrSO_4 & 0 \\ CaSO_4 + 2H_2O & 0 \end{array}\right\} \text{approximately.}$$

Many apparent anomalies in the evolution of heat would no doubt disappear if the acids and bases which take part in the reactions, as well as the resulting compounds, were soluble in water.

G. T. A.

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**Researches on the Physical Properties of Matter in the Liquid and Gaseous states under varied conditions of Temperature and Pressure.** By T. ANDREWS (Proc. Roy. Soc., xxiii, 514–521; Phil. Mag. [5], i, 78–84).

THIS investigation, which is the continuation of one on the continuity of the liquid and gaseous states of matter, was undertaken chiefly to ascertain the modifications which the three great laws, discovered

respectively by Boyle, Gay-Lussac, and Dalton, undergo when matter in the gaseous state is placed under conditions differing greatly from those already observed.

The apparatus employed is in all essential parts similar to that described in the paper referred to, the chief improvements being the method of ascertaining the original volumes of the gases before compression, and also in the mode of preparing the leather washers used in the packing of the fine screws by means of which the pressures are obtained. These washers are now prepared by heating them in a vacuum under melted lard; these never fail provided they are used in a vessel filled with water, but have always yielded in an iron apparatus when filled with mercury, even at a pressure not greater than 40 atmospheres. The author hopes that in a short time he will be able to construct an apparatus by which the rate of compressibility of hydrogen or other gases may be determined by direct reference to the weight of a liquid column, or rather a number of liquid columns, up to pressures of 500 or even 1,000 atmospheres. For the present the results are deduced from the apparent compressibility of hydrogen or air contained in capillary glass tubes.

*Liquefaction of* $CO_2$ *Gas.*—The following results have been obtained from a number of observations, the pressures having been measured by an air manometer. The two results (for 13·09° and 21·46°) recorded in the former paper agree closely with these later experiments. The pressures the author has found are lower than those given by Regnault (*Mémoires de l'Académie des Sciences*, xxvi, 618), but he thinks that the method employed by that distinguished physicist would not lead to accurate results, on account of the small quantity of compressed air contained in the Thilorier's apparatus in which they were conducted.

*Law of Boyle.*—The author has now finished a long series of experiments on the compressibility of $CO_2$ at the respective temperatures of 6·7°, 63·7°, and 100° centigrade. The two latter temperatures were obtained by passing the vapours of methyl alcohol and water respectively into the rectangular case surrounding the apparatus; at the lower temperature of 6·7° the results were limited by the occurrence of liquefaction, but at the higher temperature the pressures were carried up to 223 atmospheres. In the following extracts from the author's table, $p$ denotes the pressure in atmospheres given by an air manometer; $t'$, the temperature of the $CO_2$; $\epsilon$, the ratio of the volume of the $CO_2$ under one atmosphere and at the temperature $t'$, to its volume under the pressure $p'$ and at the same temperature; and $\theta$ the volume to which one volume of $CO_2$ measured at 0° and 760 mm. is reduced at the pressure $p$ and temperature $t'$.

*Carbonic acid at 6·7°.*

| $p$. | $t'$. | $\epsilon$. | $\theta$. |
|---|---|---|---|
| 13·22 | 6·90° | $\frac{1}{14·36}$ | 0·07143 |
| 40·11 | 6·59° | $\frac{1}{58·40}$ | 0·01754 |

*Carbonic acid at 63·7°.*

| $p$. | $t'$. | $\epsilon$. | $\theta$. |
|---|---|---|---|
| 16·96 | 63·97° | $\frac{1}{17·85}$ | 0·06931 |
| 222·92 | 63·82° | $\frac{1}{446·9}$ | 0·00277 |

*Carbonic acid at 100°.*

| | | | |
|---|---|---|---|
| 16·80 | 100·38° | $\frac{1}{17·33}$ | 0·07914 |
| 223·70 | 99·44° | $\frac{1}{380·9}$ | 0·00359 |

From these results it appears that at 60·7° $CO_2$ gas under 223 atmospheres is reduced to $\frac{1}{447}$ of its volume, or to less than $\frac{1}{2}$ the volume it should occupy if it contracted in conformity to Boyle's law. Even at 100° the contraction under the same pressure amounts to $\frac{1}{381}$ of the whole.

*Law of Gay-Lussac.*—The results obtained with $CO_2$ show that this law, like Boyle's, is true only in certain limiting conditions of gaseous matter, and that it wholly fails in others. It is shown that not only does the co-efficient of expansion change rapidly with the pressure, but that, *the pressure or volume remaining constant, the co-efficient changes with the temperature.* This latter result was first obtained for preliminary experiments under a pressure of 17 atmospheres at temperatures 4°, 20°, and 54°. The experiments were conducted by the two methods commonly known as the method of constant pressure and the method of constant volume.

*Expansion of Heat of Carbonic Acid Gas under High Pressures.*

| Pressure at | Vol. $CO_2$ at 0° and 760 mm. = 1. | Vol. $CO_2$ at 6·05° and 22·26 at. = 1. | Temperature. | |
|---|---|---|---|---|
| 22·26 | 0·03934 | 1·0000 | 6·05° | (A). |
| 22·26 | 0·05183 | 1·3175 | 63·79° | |
| 22·26 | 0·05909 | 1·5020 | 100·10° | |

| Pressure at | Vol. $CO_2$ at 0° and 760 mm. = 1. | Vol. $CO_2$ at 6·62° and 31·06 at. = 1. | Temperature. | |
|---|---|---|---|---|
| 31·06 | 0·02589 | 1·0000 | 6·62° | (B). |
| 31·06 | 0·03600 | 1·3905 | 63·83° | |
| 31·06 | 0 04160 | 1·6068 | 100·64° | |

| Pressure at | Vol. $CO_2$ at 0° and 760 mm. = 1. | Vol. $CO_2$ at 6·01° and 40·06 at. = 1. | Temperature. | |
|---|---|---|---|---|
| 40·06 | 0·01744 | 1·0000 | 6·01° | (C). |
| 40·06 | 0·02697 | 1·5464 | 63·64° | |
| 40·06 | 0·03161 | 1·8123 | 100·60° | |

Taking as unit 1 volume of $CO_2$ at 6·05° and 22·26 atmospheres, we

obtain from series A the following values for the co-efficient of heat for different ranges of temperatures:

$$\alpha = 0{\cdot}005499 \text{ from } 6{\cdot}05^\circ \text{ to } 63{\cdot}79^\circ$$
$$\alpha = 0{\cdot}005081 \text{ from } 63{\cdot}79^\circ \text{ to } 100{\cdot}1^\circ.$$

From series B with the corresponding unit volume at 6·62° and 31·06 atmospheres, we find—

$$\alpha = 0{\cdot}006826 \text{ from } 6{\cdot}62^\circ \text{ to } 63{\cdot}83^\circ$$
$$\alpha = 0{\cdot}005876 \text{ from } 63{\cdot}83^\circ \text{ to } 100{\cdot}64^\circ.$$

From series C with unit volume at 6·01° and 40·06 atmospheres—

$$\alpha = 0{\cdot}009481 \text{ from } 6{\cdot}1^\circ \text{ to } 63{\cdot}64^\circ$$
$$\alpha = 0{\cdot}007194 \text{ from } 63{\cdot}64^\circ \text{ to } 100{\cdot}60^\circ$$

The co-efficient of $CO_2$ under 1 at. referred to a unit volume at 6° is—

$$\alpha = 0{\cdot}003629.$$

From these experiments it appears that the co-efficient of expansion increases rapidly with the pressure; between temperatures 6° and 64° it is $1\frac{1}{2}$ times as great under 22 atmospheres, and more than $2\frac{1}{2}$ times as great under 40 atmospheres as at the pressure of 1 atmosphere.

Another question of interest in reference to the laws of molecular action is the relation between the elastic force of a gas at different temperatures whilst the volume remains constant. The experiments made in this direction are only preliminary, and have been made not with pure $CO_2$, but a mixture of about 11 volumes $CO_2$ and 1 volume air. The value of $\alpha$ is, as usual, calculated from these experiments, but it must be remembered that in this case $\alpha$ no longer represents the co-efficient of volume but a co-efficient of elastic force.

From two series of experiments in series A for a unit at 13·70° and 22·70 atmospheres—

$$\alpha = 0{\cdot}004604 \text{ from } 13{\cdot}70^\circ \text{ to } 40{\cdot}63^\circ$$
$$\alpha = 0{\cdot}004367 \text{ from } 40{\cdot}63^\circ \text{ to } 99{\cdot}73^\circ.$$

In series B—

$$\alpha = 0{\cdot}0005067 \text{ from } 13{\cdot}70^\circ \text{ to } 40{\cdot}66^\circ$$
$$\alpha = 0{\cdot}004804 \text{ from } 40{\cdot}66^\circ \text{ to } 99{\cdot}75^\circ.$$

The co-efficient at 13·70° and 1 atmosphere is $\alpha = 0{\cdot}003513$. The value of $\alpha$ increases with the pressure, and is greater at lower than higher temperatures; a remarkable relation exists between the co-efficients in the present case which does not exist between the co-efficients obtained for the expansion of a gas. The values of $\alpha$ deduced, for the same range of temperatures, from the elastic forces at different pressures are directly proportional to one another thus—

$$\frac{0{\cdot}004367}{0{\cdot}004604} = 0{\cdot}9485 \text{ and } \frac{0{\cdot}004804}{0{\cdot}005067} = 0{\cdot}9481.$$

How far this relation will be found to exist under other conditions of temperature and pressure will appear on the conclusion of experiments now in progress.

*Law of Dalton.*—This law as originally enunciated by its author, held that certain elastic fluids may exist in company under any pressure and at any temperature without any regard to their specific gravities, and without any pressure upon one another. The experiments of the author upon mixtures of $CO_2$ and N have been carried on at pressures of 283·9 atmospheres as registered by a hydrogen manometer. At this pressure 3 volumes of $CO_2$ and 4 volumes of N were reduced at 7·6° to $\frac{1}{578}$, their original bulk with no liquefaction of the $CO_2$. The most important point is *the lowering of the critical point by the admixture of a non-condensable gas.* The addition of only $\frac{1}{10}$th its volume of air or nitrogen reduces the critical point of carbon dioxide several degrees. The law of Dalton, like those of Boyle and Gay-Lussac hold good only in the case of gaseous bodies at feeble pressures and at temperatures greatly above their critical points.

J. M. T.

## On the Passage of Gases through Liquid Diaphragms.

By Franz Exner (Pogg. Ann., clv, 321—336, and 443—464).

§ 1.—It has been shown by Draper, that a soap-bubble immediately expands in size on being introduced into a vessel containing carbonic acid. Marianini observed that if a soap-bubble which had been blown with air were allowed to fall into an upright cylinder partially filled with carbonic acid, it remained floating at the surface of the gas, whilst at the same time it gradually increased in size, until it became double or treble its original volume, and finally burst. A similar phenomenon was exhibited when nitrogen or oxygen was substituted for atmospheric air, and there could be scarcely a doubt but that this expansion was produced by the diffusion of carbonic acid into the interior of the bubble. Vogel and Reischauer have also made experiments in connection with this subject; they floated a thin layer of oil on the surface of a solution of indigo which had been previously reduced, and observed that the oxygen of the atmosphere exerted an oxidising influence through the layer of oil. This, however, was evidently the result, rather of the action of the absorbed gases than of the effect of diffusion.

The author of this paper has devised a very simple apparatus for the purpose of determining the rapidity with which gases diffuse through a liquid diaphragm. This apparatus consists of a glass tube, 90 mm. long and 7 mm. in diameter, one end of which is closed by a metallic plate, through which a fine thermometer-tube is cemented in such a way that the top of the tube is exactly level with the inner surface of the metallic plate. Over this thermometer-tube the end of a piece of caoutchouc tubing is fitted, and on this a clip is fastened close to the end of the thermometer tube. The glass tube has a millimeter scale affixed to it, the zero point of which is placed at the end of the tube closed by the metallic plate.

In making use of this apparatus the pinchcock is opened, and the end of the graduated tube dipped into a solution of soap. The bubble formed at the mouth is then, by gently sucking through the india-rubber pipe, drawn to a position in the tube appearing suitable for the

experiment. The clip is then closed. If the glass tube be now introduced into a bell-jar into which coal gas is being passed in a continuous stream, an alteration in the position of the diaphragm will be noticeable, and as soon as this comes to rest in its new position, the experiment is concluded.

For the determination of the relation between the rapidity of the diffusion of two gases, it is only necessary to note the position of the diaphragm at the commencement and close of the experiment; for, since the zero-point of the scale lies at that end of the tube closed by the metallic plate, the quotient of the numbers furnished by these two observations gives the required relation.

§ 2.—The soap-solution was prepared by dissolving one part by weight of dried Marseilles soap, cut into thin flakes, in from 60 to 80 parts of cold distilled water. After the lapse of from 1½ to 2 hours, all the particles remaining undissolved were removed, and the solution was then allowed to stand for 3 or 4 days in a tall cylinder, when all the insoluble portion having settled to the bottom in the form of a flocculent precipitate, the clear solution was removed by a siphon, and was ready for use. The dilution of this soap-solution with more or less water, or even the addition of glycerin, was found to be without influence on the results of the experiments; this, however, is not necessarily true of other substances, as alcohol, for example. In the following experiments the author used a soap-solution prepared in this way, but without any addition whatever:—

(I.) The first experiments were made with air and coal-gas, in the manner already described, but with this modification, which was also adopted in all succeeding cases, that instead of introducing the graduated tube containing the liquid diaphragm into a bell jar of the gas to be diffused, this was simply conducted in a continuous stream, by means of a tube 3 or 4 mm. wide, into the graduated tube, which in the present case was of course supported with its open end downwards.

The following figures show the results of one of the experiments:—

| Position of the Diaphragm in mm. of the scale. | Time in minutes from the commencement of the experiment. |
|---|---|
| 19·0 | 0 |
| 33 0 | 4 |
| 36·5 | 6 |
| 40·2 | 10 |
| 42·0 | 16 |
| 41·0 | 19 |

It will be seen that, at the commencement of the experiment, the diaphragm stood at 19·0 mm., and had reached its furthest position at 42·0 mm. The quotient 42 : 19 will therefore represent the ratio between the rapidity with which coal-gas and air pass through the diaphragm in equal spaces of time, and if we call this $a$, then

$$a = 2{\cdot}21.$$

That is, the rapidity of the diffusion of coal gas is exactly 2·21 times greater than that of air.

The supply of coal gas having now been discontinued, the enclosed gas was allowed to diffuse out into the air, so that the retrogade movement of the diaphragm could be observed. The result of this observation was as follows :—

| Position of the Diaphragm. | Time in minutes |
|---|---|
| 42·0 | 0 |
| 36·0 | 1 |
| 21·8 | 3½ |
| 19·0 | 7 |
| 18·4 | 10 |
| 18·2 | 12 |
| 18·2 | 14 |

This gives a somewhat higher result, viz. :—

$$a = 2{\cdot}31.$$

Other trials were made with the diaphragm at different positions in the tube at the commencement, and the results were in each case concordant, thus proving the value of $a$ to be in no way dependent upon the original volume of air in the diffusion tube.

Results are given of 31 experiments, the mean of which shows the value of $a$ to be 2·27.

(II.) Experiments were made in the same way with hydrogen and air, and the mean of 17 results gives 3·77 as the value of $a$, *i.e.*, 3·77 volumes of hydrogen diffuse through the diaphragm into the enclosed space for each volume of air which passes out.

(III.) The next gas experimented upon was carbonic acid, but in this case the method hitherto employed was found to be impracticable, as the diaphragm invariably burst, on account of the rapidity with which it was forced to move, owing to the great swiftness with which this gas passed through into the enclosed space.

On account of this difficulty presenting itself, another method had to be devised, and the following plan was adopted, although the results were not so exact as those obtained by the former process. The soap-solution was poured to about the depth of 5 mm. into a shallow dish, at the bottom of which a millimeter scale was so affixed that the graduations could be easily seen through the liquid. Bubbles of carbonic acid were then blown on the surface of the soap-solution, and their diameter observed by means of the scale at the bottom of the dish. On account of the short duration of the experiment, it was, however, only possible to make three or four observations.

The following figures show the result of one of the experiments made in this manner :—

| Diameter of the bubble in mm. | Time in minutes. |
|---|---|
| 26 | 0 |
| 10 | ½ |
| 7 | 1 |

Therefore $a = 51{\cdot}2$.

From the mean of 15 experiments, the value of $a$ is shown to be in this case 47·1.

(IV.) Sulphuretted hydrogen gas was then experimented upon, the same method being used as that employed in the preceding case. The mean of 12 determinations gave 165 as the value of $a$.

(V.) The same method was employed in experiments with ammonia, and to prevent any absorption by the soap-solution, this was previously saturated with the gas. The results of these experiments gave the extraordinarily high number 46,000 as the value of $a$.

(VI.) Oxygen gas was experimented upon in the graduated tube apparatus, and the value of $a$ was found to be 1·95.

(VII.) The rate of diffusion of nitrogen gas was also determined in the tube apparatus, and the value of $a$ found to be 0·86.

(VIII.) A control experiment was made with coal gas and oxygen, and the result showed that in exchange for each volume of coal gas, 0·83 volumes of oxygen passed through the diaphragm. Now in the former experiments (I and VI) the coefficients of the diffusion of oxygen and coal gas compared to air have been shown to be 1·95 and 2·27 respectively. The coefficient of oxygen compared to coal gas would therefore be $\frac{1{\cdot}95}{2{\cdot}27} = 0{\cdot}86$, which agrees as well as can be expected with that found by direct experiment, viz., 0 83.

(IX.) In the same way a control experiment was performed with coal gas and hydrogen, the result being 1·64, the coefficient obtained by calculation from the data furnished by the previous experiments being 1·65.

(X.) A similar experiment was also made with nitrogen and hydrogen, the result of which gave the quotient 4·12 against 4·38 obtained by calculation.

(XI.) *Determination of the rapidity with which Gases pass through the Diaphragm.*—The results of the former experiments have shown merely the rate of rapidity of the passage of different gases compared with air. The author sought next to determine the actual rate of the diffusion of each gas.

A graduated diffusion tube was attached by a caoutchouc connection to a large flask; a diaphragm of soap-solution was introduced, and the experiments conducted as before by passing a continuous stream of the gas to be diffused into the tube containing the diaphragm. As the air contained in the flask was very great in proportion to the volume of the gas diffusing into it, it was easy to make several observations before sufficient of the latter had passed into the flask to interfere with the uniformity in the rate of diffusion. It was of course necessary to be extremely careful that the air in the flask suffered no change in temperature during the experiment.

From observations of the onward movements of the diaphragm in successive intervals of time, the value of $a$ being known, it is easy to calculate the rate of the diffusion of each gas. For if $v$ be the cubic space through which the diaphragm moves in a minute of time, and V and V′ the respective volumes of each gas passing through the diaphragm per minute, then $v = \mathrm{V} - \mathrm{V}'$. But in the former experi-

ments the relation $\frac{V}{V'}$ has been expressed by $a$. Therefore from the two equations

$$v = V - V'$$

and

$$\frac{V}{V'} = a$$

we get

$$V = \frac{av}{a - 1}$$

and

$$V' = \frac{v}{a - 1}.$$

In the actual experiments the volume of air in the flask measured about 4 litres; the diffusion-tube had a length of 180 mm, and measured 10·5 mm. in diameter; the base was therefore 86·5 square millimetres.

The first experiment was made upon coal gas, and the results show the movement of the diaphragm to have been at the uniform rate of 8·17 mm. per minute. It consequently follows that

$$v = 8{\cdot}17 \times 86{\cdot}5 \text{ c. mm} = 706{\cdot}7 \text{ c.mm.}$$

and therefore that $V - V' = 706{\cdot}7$ c mm.

But it has been shown (I) that $\frac{V}{V'} = a = 2{\cdot}27$,

therefore $V = 1{\cdot}263$ c c.

and $V' = 0{\cdot}556$ c.c.

Or calculating these results for a diffusion surface of 1 square centimeter, and calling the volumes $\phi$ and $\phi'$ respectively, we obtain

$$\phi = 1{\cdot}46 \text{ c.c.}$$

and

$$\phi' = 0{\cdot}64 \text{ c.c.}$$

The details of similar experiments made with hydrogen gas are also given.

§ 3.—It will be observed that the foregoing experiments indicate no distinct relation between the rapidity of the diffusion of a gas and its density. A certain connection, however, can be established between the rapidity of diffusion and the coefficient of absorption. This will be seen from a comparison of the numbers in the following Table:—

| Gas. | $a$. | Coefficient of absorption. |
|---|---|---|
| N | 0·86 | 0·015 |
| Air | 1 | 0·016 |
| O | 1·95 | 0·030 |
| Coal gas | 2·27 | 0 025 |
| H | 3·77 | 0 019 |
| $CO_2$ | 47·1 | 1 002 |
| $H_2S$ | 165 | 3·165 |
| $NH_3$ | 46000 | 700 |

An irregularity will be noticed in the case of hydrogen, and since this gas differs so considerably in density from the other gases, it was considered possible that diffusion of this kind through a liquid diaphragm might be connected, not merely with absorption, but also with that kind of diffusion which takes place through solid bodies.

Supposing the passage of a gas through the diaphragm to be the result on the one hand of transmission by absorption, and on the other hand of ordinary diffusion, as would happen in the case of a porous diaphragm of extremely minute thickness, then the rapidity of the passage of a gas would be proportional to the expression, $\frac{c}{\sqrt{\delta}}$, where $c$ is the coefficient of absorption, and $\delta$ the density of the gas.

The following Table shows that this closely agrees with the experimental results:—

| Gas. | Coefficient of absorption. | Density. | $\frac{c}{\sqrt{\delta}}$. | $a$ observed. | $a$ calculated. |
|---|---|---|---|---|---|
| N | 0·015 | 0·97 | 0·0153 | 0·86 | 0·85 |
| Air | 0·017 | 1·00 | 0·017 | —— | 1·00 |
| O | 0·030 | 1·106 | 0·0285 | 1·95 | 1·60 |
| Coal gas | 0·025 | 0·480 | 0·036 | 2·27 | 2·12 |
| H | 0·019 | 0·070 | 0·072 | 3·77 | 3·89 |
| $CO_2$ | 1·002 | 1·52 | 0·812 | 47·1 | 45·1 |
| $H_2S$ | 3·165 | 1·17 | 2·94 | 165 | 163·3 |
| $NH_3$ | 700 | 0·59 | 903·0 | 46000 | 54450 |

H. H. B. S.

## Effects of Powder in Fire Arms. By E. Sarrau (Compt. rend., lxxxii, 898—899).

This paper relates to mathematical formulæ by which the velocity of a projectile and the maximum internal pressure in the powder chamber of the gun may be deduced from the following data:—1st. The heat of combustion of the powder. 2nd. The volume of permanent gases produced. 3rd. The rapidity of combustion in the open air.

R. R.

## An Air Thermometer. By A. Mitscherlich (Chem. Centr., 1875, 673).

The bulb may be of infusible glass, or, when necessary, of platinum, and the tension of the air within it is indicated by the height of a column of mercury, which is sustained in a long, narrow, vertical tube, hermetically sealed at the top, and connected with the bulb by a shorter and wider horizontal tube. The atmospheric pressure is thus eliminated, so that this thermometer may be read like an ordinary instrument.

R. R.

# Inorganic Chemistry.

**Salt Solutions and Attached Water.** By FREDERICK GUTHRIE (Phil. Mag. [5], i, 49—60).

IN the first part of this paper the author begins by discussing the behaviour of certain peculiar salts, as cryogens and cryohydrates.

*Chloride of Calcium as a Cryogen.*—The crystallised salt, $CaCl_2 + 3H_2O$ was used. The greatest amount of cold was produced by mixing 38·5 of ice or snow with 61·5 of the crystallised salts. This is the ratio between $CaCl_2.3H_2O$ and 5·74 $H_2O$, or $4(CaCl_2.3H_2O)$ and 23 $H_2O$, or $CaCl_2$ and 8·74 $H_2O$.

*Anhydrous Chloride of Calcium as a Cryogen.*—Freshly fused chloride was finely powdered and mixed with ice. In this case the lowest temperature is reached at the ratio of 1 : 4, or about $CaCl_2 + 15H_2O$. The author does not attach too much importance to these results, on account of the liberation of heat in dissolving the anhydrous chloride.

*The Cryohydrate of Calcium Chloride.*—A solution of $CaCl_2.3H_2O$ was saturated at 10°, then cooled in snow and ice to − 20°, and the mother-liquor exposed to the carbonic acid and ether cryogen, when the temperature sank to − 37°, at which point an opaque cryohydrate forms. The crystals on being re-melted showed the following composition. By a silver determination, 6·6835 contained 2·3365 $CaCl_2$, this showing 36·45 of $CaCl_2$ exhibits the molecular ratio of $CaCl_2 + 11·8\ H_2O$.

*Mixed Nitrates of Potassium and Sodium as Cryohydrates.*—The two salts were weighed in molecular ratios: thus $KNO_3$ = 33·666 grms. and $NaNO_3$ = 28·333 grms.; the quantities after solution in water were allowed to evaporate at 13°, till crystallisation began, the mixture being then cooled in an ice-salt cryogen. At about + 12° to + 10°, white crystals resembling $KNO_3$ began to form; at − 7° an opaque cryohydrate appeared; at − 10° the mass became pasty; at − 145° nearly dry; and at − 17°, quite dry. From these data the author finds that—

| | | | |
|---|---|---|---|
| The cryohydrate of | $KNO_3$ | solidifies at | − 2·7°. |
| ,, ,, | $NaNO_3$ | ,, | − 17·5°. |
| ,, ,, | equiv. mixture | | − 7° to − 17°. |

*Mixed Chlorides of Potassium and Sodium as Cryogens and Cryohydrates.*—The salts taken in molecular proportions (KCl = 18 625 and NaCl = 14·625) were dissolved in water, and allowed to stand till crystallisation began, when a solution was obtained, solidifying completely at − 21° C. The same mixture of the salts when mixed with ice gave a resulting temperature of − 21·8°. In these cases the temperatures are evidently governed by the action of the NaCl.

*Mixed Chlorides of Potassium and Ammonium as Cryohydrates and Cryogens.*—Of ammonium chloride, 13·375 grms., and of potassium chloride, 18·625 grms. were taken, dissolved, mixed, and allowed to evaporate till crystallisation began. On cooling, solidification did not

begin till — 16·5° to — 17°, and on reaching — 18° the whole mass became solid. The analyses of the re-melted last crop of cryohydrate were made, the percentage composition being—

| | a. | b. | Mean. |
|---|---|---|---|
| KCl ..... | = 12·12 | 12·04 | 12·08 |
| $NH_4Cl$ ..... | = 11·43 | 11·55 | 11·49 |
| $H_2O$ ..... | = 76·45 | 76·41 | 76·43 |

These give the following molecular relations for the cryohydrate, $3KCl + 4NH_4Cl + 79·2\ H_2O$. As the author has shown in a previous paper that the water-worth of $NH_4Cl$ is 12·2, and that of KCl 16·61, this compound body cannot be looked upon as a mixture of the two cryohydrates, but may, perhaps, be regarded as consisting of seven molecules of cryohydrate of ammonium chloride, in which three molecules of ammonium are replaced by potassium. The possible precision in the analyses of mixed chlorides of ammonium and potassium caused the author to extend the examination to the intermediate crop of cryohydrates; from these it appears that the successive crops are nearly unchanged; the later the crop, the poorer it is in water and potassium, and richer in ammonium. The same ratio of the same chlorides used as a cryogen gave a temperature of — 18°.

*Mixed Nitrates of Barium and Strontium as Cryohydrates and Cryogens.*—Of strontium nitrate, 7·05 grms.. and of barium nitrate, 8·70 grms. were dissolved and allowed to evaporate to incipient crystallisation. At — 1·2° a cryohydrate began to form, the whole becoming solid at — 4·3°. Employed as a cryogen, the mixture gave — 5·8°.

*Mixed Chlorides of Barium and Strontium as Cryohydrates and Cryogens.*—Equivalent proportions of the salts were dissolved and evaporated to saturation. On cooling at — 10°, a cryohydrate began to form, and the whole was nearly solid, at — 13·5° to — 14 . Mixed with snow, the salts in the above proportions lower the temperature to — 16° 7.

*Mixed Sulphates of Sodium and Ammonium as Cryohydrates and Cryogens.*—Of ammonium sulphate, 6·6 grms., and of sodium sulphate, 7·1 grms. were taken, dissolved, and evaporated to saturation. The cryohydrate began to form at — 4·5°, the whole being solid and dry at — 7°. The following is the mean of the last analyses of the portion last solidified $(NH_4)_2SO_4 = 12·24.Na_2SO_4 = 4·84$, $H_2O = 82·92$. The molecular ratios are therefore $Na_2SO_4 = 1.(NH_4)_2SO_4 = 2·72.H_2O$. 135·2, or nearly $4Na_2SO_4 + 11(NH_4)_2SO_4 + 541\ H_2O$.

As it has been previously shown that the water-worth of $Na_2SO_4$ is 165·6, and that of $(NH_4)_2SO_4$ is 10·2, this cryohydrate cannot be regarded as a substitutive cryohydrate, like that suggested in § 113°, or as a simply additive cryohydrate, for the joint water-worth is less than that of the ammonium salt alone. The double sulphate of sodium and ammonium is formed, and has the specific water worth of 135·2, or taking the higher molecule, 541.

*Variation of both Constituents* (AX + BY).—The author thinks that Berthelot's hypothesis regarding the occurrence of partial double

decomposition when two salts, AX and BY, are mixed, even when no removal from the chemical field takes place of any of the possible resulting bodies, may be examined from the side of the cryohydrate. Is a solution of $KNO_3$ 202 grms., and $Na_2SO_4$ 142 grms., identical with a solution of $NaNO_3$, 170 grms., and $K_2SO_4$ 174 grms. dissolved in the same amount of water?

*Comparison between a Mixture of* $2(NaNO_3)$ *and* $K_2SO_4$, *and a Mixture of* $2(KNO_3)$ *and* $Na_2SO_4$.—The salts (anhydrous) were dissolved and evaporated to saturation. On cooling, the solutions showed the same behaviour throughout, solidifying to dryness at $-5°$. The author thinks that there is nothing in their behaviour to disprove their identity, and in comparing this experiment with those already mentioned, proof to a certain extent is given, not that there are four salts in the two solutions, but that there are none of the original salts in either, because it is seen that AX and BY being mixed, the temperature of final solidification is in no case sensibly above that required for the solidification of that constituent whose solidification takes place at the lowest temperature. Thus had $NaNO_3$, either original or devised, been in the solution, final solidification would have taken place at above $-17°$, instead of $-5°$. In another case the author has taken two solutions, not in equivalent quantities:—

A. $66Na_2SO_4$ and $87·72$ $KNO_3$.

B. $91K_2SO_4$ and $85·00$ $NaNO_3$. In this case solidification took place at $-5°$, and in the last portions sulphuric acid was determined; A gave 20·3 per cent. $SO_3$, and B, 18·8 per cent. $SO_3$.

The author concludes his paper with a table, giving the results of mixtures of salts as cryohydrates and cryogens, as compared with the behaviour of their constituents in the same capacity. On comparing the results given in the table, the author concludes that nitrates of the alkalis and alkaline earths act together, but not as double salts; chlorides may act in union with each other, or with sulphates; sulphates may act together, or with chlorides or nitrates. The agreement in composition, pointing to the relation, $3KCl + 4NH_4Cl$, shows that these chlorides have mutual equivalents, which if not in simple relation to their so-called atomic weights, are yet definite and constant.

J. M. T.

## Ozone in Atmospheric Air. By M. Marié-Davy (Compt. rend., lxxxii, 900—902).

The author has, with very satisfactory results, employed a mixture of solutions of potassium iodide and potassium arsenite for estimating ozone in the atmosphere. After 250 litres of air per hour had been passed for 12 hours through two vessels in succession, each containing 20 c.c. of the titrated liquid, the reaction was found to have taken place entirely, or nearly so, in that vessel through which the air first passed. It was also found that the ammonium nitrite present in the air did not affect the indications.

R. R.

## The Explosion of Gunpowder. By M. BERTHELOT (Compt. rend., lxxxii, 469—475).

FROM the opinion of Noble and Abel, that the transformations which occur in the explosion of gunpowder do not admit of definite chemical representation, the author dissents. He adduces five equations, representing regular reactions, which, being supposed to affect simultaneously certain proportions of the materials, would correspond approximately with the analytical results. He considers that the explosion always gives rise to potassium sulphide, sulphate, and carbonate, and to carbonic oxide, nitrogen, and aqueous vapour; but that the relative proportions of these, the chief products, vary with the particular circumstances of the mixture and manner of inflammation.

R. R.

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## Absorption of Ammonia Gas by Calcium Sulphate. By E. H. JENKINS (J. pr. Chem. [2], xiii, 239).

ANHYDRITE does not absorb ammonia gas either at ordinary temperatures or at 50° and 100°. So also native gypsum, as well as calcium sulphate (precipitated by sulphuric acid from calcium chloride), with their normal amount of water of crystallisation, show no absorption either at ordinary temperatures or at 50°. When, however, these substances have lost a part of their water of crystallisation by a gentle heat, they become capable of absorbing ammonia in small quantities. Elevation of temperature increases the absorption The ammonia absorbed is scarcely or very slowly given up when air at the ordinary temperature is passed over the body.

G. T. A.

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## On the Exchanges of Ammonia between Natural Waters and the Atmosphere. By TH. SCHLOESING (Compt rend., lxxxii, 846—849, and 969—972).

THE application to natural phenomena of the theories developed in the author's previous papers.

C. H. P

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## Action of Sulphuric Acid on Tricalcic Phosphate. By H. P. ARMSBY (J. prakt. Chemie [2], xiii, 333—336).

IT appears from the author's experiments that the reaction between equal molecules of tricalcic phosphate and sulphuric acid takes place in two separate stages:

I. The sulphuric acid acts upon half the phosphate, forming soluble phosphate, $CaH(PO_4)_2$, thus:—

$$Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4$$

II. The phosphate, $CaH_4(PO_4)_2$, then reacts upon the other half of the tricalcic phosphate, producing the insoluble phosphate, $CaHPO_4$, thus:—

$$CaH_4(PO_4)_2 + Ca_3(PO_4)_2 = 4CaH(PO_4).$$

H. H. B. S.

## On the Crystals formed in the Cells of Leclanché's Battery.

By E. PRIWOZNIK (Deut. Chem. Ges. Ber., ix, 612—615).

THE author has again examined these crystals, and finds them to have the composition represented by the formula $ZnCl_2(H_3N)_2$, as previously stated by him. The crystals are prismatic, and not quadratic, as stated by Davis (*Chem. News*, 1872, 265), who, moreover, assigns to them the formula $ZnH_2O_2.NH_4Cl$. Priwoznik thinks that Davis must have analysed crystals partially altered by contact with water.

J. R.

## Bismuth and Iron Salts.

By R. ROTHER (Pharm. J. Trans. [3], vi, 764).

BISMUTHOUS citrate may be prepared by heating bismuthous oxynitrate with an equivalent quantity of a concentrated solution of citric acid; the crystalline precipitate formed is anhydrous, having the formula $Bi'''C_6H_5O_7$; from this the ammonio-citrate $(NH_4)_3C_6H_5O_7Bi(HO)_3$, may be obtained by heating it with ammonia solution, ferric citrate heated with ammonia yields ammonio-ferroxycitrate $(NH_4)_3C_6H_5O_7Fe(OH)_3$. The existence of di- and mono-ammonioferric citrates has been ascertained, both being acid salts, which, when treated with ammonia in excess, deposit ferric hydrate. Bismuthous citrate may be retained in an acid solution provided that ammonio-ferric citrate be also present, the two probably forming a double salt of the constitution $Fe'''(NH_4)_3 2C_6H_5O_7.Bi(OH)_3$.

E. W. P.

## On Vanadium.

By ANTHON GUYARD (HUGO TAMM) (Bull. Soc. Chim [2], xxv, 350—356).

THE methods for obtaining vanadium compounds in the wet way are not very well known. The methods adopted by the author are briefly given as follows.

*Vanadious oxide* is best prepared in a perfectly pure state by igniting vanadious chloride in a porcelain crucible. It can also be obtained by igniting vanadious oxalate.

*Vanadious chloride* is prepared by dissolving vanadic acid in warm hydrochloric acid: chlorine is evolved, and as a portion of the vanadic acid still remains undissolved, a small quantity of alcohol is added towards the end of the reaction, when the vanadic acid residue dissolves immediately. The solution is then filtered in order to remove a little silica (unavoidably present), and evaporated down to dryness on a water-bath. The dry salt is deliquescent and almost soluble in water.

*Vanadious Bromide.*—Easily obtained by treating vanadic acid with bromine-water mixed with bromine and an alcohol. A very energetic reaction takes place. If methylic alcohol be used, an organic brominated compound is evolved which exerts a very irritating action upon the eyes. Vanadious bromide resembles the chloride very closely, but it easily decomposes, leaving a residue of vanadious oxide. In order to

obtain the salt dry, it is evaporated down carefully at a temperature not exceeding 80°. Vanadious bromide can also be obtained by treating vanadious oxide with hydrobromic acid.

*Vanadious iodide* is obtained by treating vanadious oxide with hydriodic acid. Closely resembles vanadious chloride and bromide. The dry salt is an amorphous mass of a dark green, almost black, colour. It decomposes easily.

*Vanadious Fluoride.*—Prepared by treating vanadic acid contained in a platinum basin with hydrofluoric acid and alcohol. Its dilute solution is blue, but the concentrated solution is green. Can be evaporated to dryness without decomposition, and also dried at a high temperature without decomposing, becoming an amorphous dark green mass. At a red-heat, it splits up into hydrofluoric acid and vanadious oxide; thick yellow fumes of anhydrous vanadium fluoride being evolved at the same time.

*Vanadious nitrate* may be obtained in solution only (as all the vanadium separates out as vanadic acid on evaporating the solution), by precipitating vanadious chloride with silver nitrate, or vanadious sulphate with barium nitrate.

*Vanadious sulphate* can be prepared either by acting on vanadic acid with a mixture of sulphuric acid, water, and alcohol, or by treating a solution of sulpho-vanadic acid with alcohol. In either case, a beautiful blue liquid is obtained, which, on evaporating to dryness, leaves an amorphous blue mass completely soluble in water. On igniting this sulphate (not in contact with the air), vanadious acid is left behind.

*Vanadious Fluosilicate.*—Prepared by boiling vanadic acid with fluosilicic acid and alcohol. On concentrating the blue solution, it becomes green, and eventually, on carrying on the evaporation to dryness, a grey deliquescent amorphous mass remains, which is completely soluble in water. Vanadium does not appear to form true double salts with the alkalis.

*Organic Salts of Vanadium.*—Vanadious salts containing a volatile organic acid can best be obtained by acting upon vanadious sulphate with barium formate, acetate, &c. The solutions thus obtained, on being evaporated to dryness, generally give rise to amorphous masses, soluble in water. Those salts which contain a fixed organic acid are all prepared by melting the fixed acid in its water of crystallisation with vanadic acid, until a reaction occurs, and the mass assumes a greenish-blue or dark green colour, and is perfectly soluble in water.

*Vanadious oxalate* is thus prepared in a few minutes. The blue solution in water of the mass obtained furnishes crystals of vanadious oxalate.

*Vanadious tartrate, citrate,* and *succinate* were prepared in the same way. They are all soluble in water, and on evaporating the solutions to dryness, gummy amorphous masses are obtained.

*Salts in which Vanadium Pentoxide Acid acts as a Base.—Vanadic Sulphate.*—Prepared by heating sulphuric acid together with vanadium pentoxid, and evaporating to perfect dryness. The resulting salt is an amorphous mass possessing a chamois colour, and furnishing a reddish-yellow solution in water.

*Vanadic Pyrophosphate.*—Formed by fusing the pentoxide acid with vitreous phosphoric acid. It is a pale yellow glass containing a great deal of vanadic acid, and quite soluble in water.

*Vanadic Borate.*—Obtained in the same way as the pyrophosphate, which it closely resembles. Soluble in water. It can be crystallised, but the salt easily decomposes with the separation of boric acid.

VANADATES.—The author has nothing new to say about the vanadates, except that:

*Ammonium divanadate* is best prepared by adding acetic acid to a solution of ammonium vanadate and evaporating the solution down at a very low temperature (50°—60°) until the point of crystallisation is reached. The salt crystallises in large transparent crystals, very like those of potassium bichromate.

*Vanadium-bronze.*—The preparation known by this name is ammonium vanadate. On heating it in a sealed tube, ammoniacal fumes are evolved, and a residue of vanadious oxide in black crystalline scales remains behind. Vanadium-bronze is, therefore, not a metavanadate.

C. A. B.

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## Chemical Constitution of Manganese Compounds.

By H. LASPEYRES (J. pr. Chemie [2], xiii, 176—215).

THIS paper, which is much too long for abstraction, proposes a new classification of the compounds of manganese, referring them to twelve different types, which all contain manganic acid, $H_2MnO_4$ + a certain amount of water. In these the manganese, which the author holds to be bivalent, plays the part of a base or an acid-radicle. Peroxide of manganese, for instance, is termed manganomanganate, $mnMnO_4$—the mn being basic—and belongs to type I, $H_2MnO_4$. Type II is derived from normal manganic acid, + $\frac{2}{5}$ of a molecule of water —$H_2MnO_4$ + $\frac{2}{5}H_2O$, and is termed five-sevenths manganic acid—$H_{14}Mn_5O_{22}$. The manganomanganate of this type is $mn_7Mn_5O_{22}$. Under type VII, $H_6MnO_6$ (= $H_2MnO_4$ + $2H_2O$) comes varvicite, $H_2mn_2MnO_6$, and braunite, $mn_3MnO_6$. Wad is referred to type X, $H_{10}MnO_8$ (= $H_2MnO_4$ + $4H_2O$), and is written $H_6Mn_2MnO_8$. Crednerite ($3CuO.2mn_2O_3$) becomes, under type XI ($H_{12}mnO_9$ = $H_2MnO_4$ + $5H_2O$)$Cu_3mn_4MnO_9$. A lengthy appendix gives additional reasons in favour of the bivalence of manganese.

G. T. A.

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## Constitution of the Aluminous Ores of Manganese.

By H. LASPEYRES (J. pr. Chem. [2], xiii, 215—236).

THE object of the paper is to show that the aluminium replaces part of the basic manganese in several minerals, forming compounds, the constitution of which supports the author's views of the compounds of manganese as given in the previous paper.

G. T. A.

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## Composition of the Native Peroxides of Manganese.

By T. L. PHIPSON (Bull. Soc. Chim. [2], xxv, 439).

THE composition of the manganese peroxides in commercial use varies considerably, certain samples containing fluorine and phosphoric acid in tolerable quantities. Very dilute nitric acid acting for 24 hours upon a variety much used in England, gave a solution which contained much phosphate of lime; a little arsenic acid, traces of nickel and cobalt, much iron and traces of indium, lead, and copper. Boiling hydrochloric acid leaves a reddish residue consisting of silicate of manganese.

C. H. P.

## Preparation of Platinum. (Dingl. polyt. J., ccxx, 95.)

SINCE Deville and Debray's *dry* method of preparing platinum has not been successful in the platinum-industry, the *wet* method is still preferred. At the St. Petersburgh Mint, Döbereiner's method was used, which is based on an assumption that platinum chloride cannot be precipitated from solutions by lime in the dark. But this assumption has been shown to be incorrect; the platinum is in fact partly precipitated, and that which is left in solution is mixed with iridium. Schneider's method (*Dingler*, cxc, 118) seems to give better results.

J. Philipp describes the following method, which is used at Heräus' works in Hanau:—The ore is dissolved in one part of aqua regia and two parts of water in glass retorts under a pressure of 314 mm. water. The solution is evaporated, and the dry mass heated to 125°, at which temperature the palladium and iridium salts are reduced to subchlorides. The solution acidified with hydrochloric acid is treated with sal-ammoniac which throws down pure platinum-sal-ammoniac, while iridium-sal-ammoniac separates after evaporating the mother-liquors. In the filtrate from the platinum precipitate the metals are precipitated with iron turnings; the precipitate is freed from the excess of iron with hydrochloric acid and again dissolved in aqua regia, and from the solution another portion of platinum and iridium salts is obtained. The spongy platinum obtained by fusing the platinum-sal-ammoniac is pressed, then broken into lumps, and fused in a lime crucible with oxygen.

Most of the platinum, when brought into commerce, is not pure, but often contains as much as 2 per cent. of iridium, an admixture which renders platinum more suitable for vessels, &c.

The other metals—palladium, rhodium, ruthenium, osmium, and iridium—which accompany platinum, are prepared by evaporating the mother-liquors, when the iridium separates out with traces of platinum. After allowing the concentrated liquor to stand, the precipitate is filtered off, and the solution, after diluting, precipitated with zinc. The precipitate is digested with hydrochloric acid, washed and fused. Aqua regia dissolves from the mass the palladium and a small quantity of gold, leaving impure rhodium behind. The solution is saturated with ammonia, and the palladium precipitated with hydrochloric acid. The residue left on dissolving the platinum, which in Russian platinum

amounts on an average to 8 per cent., is fused, ground and washed. The dust is fused with equal parts of borax and saltpetre, and after treatment with hydrochloric acid and water, the platinum metals remain behind. These are alloyed with double the quantity of zinc in a graphite crucible, and the alloy is freed from the zinc by hydrochloric acid. The mass is then treated with chlorine in tubes made of Hessian clay with glass receivers; in this manner iridium and osmium chlorides are obtained. From the residue left after fusing in a stream of hydrogen, ruthenium is extracted by fusion with caustic potash and saltpetre.

D. B.

## Mineralogical Chemistry.

### The occurrence of Nitride of Iron amongst the "Fumarole Products" of Etna, and its Artificial Preparation. By ORAZIO SILVESTRI (Pogg. Ann., clvii, 165—172).

ON being passed through a red-hot platinum tube, ammonia gas splits up, as is well known, into its elementary constituents, which pass mixed together out of the tube. On repeating this experiment with a platinum tube filled with pieces of Etna lava, and igniting it strongly, the author observed that a great part of the nitrogen remained behind combined with the lava, whilst the hydrogen was liberated.

By substituting hydrochloric acid gas for the ammonia gas, the lava was vigorously attacked and acquired a yellow colour, owing to the formation of ferric chloride; and on dissolving this in water, a white insoluble substance remained behind which proved to be silica. This experiment explains firstly, the formation of the enormous masses of ferric chloride found on the newer lavas and in the openings and clefts of the fumaroles, also in the interior crater; and secondly, the presence of powdery silica, which gives a white colour to the lava, after the rain has dissolved out the ferric chloride. The author further discovered on heating lava (which had been thus attacked by hydrochloric acid gas and carefully dried) at a high temperature in a glass or porcelain tube, and passing through it a stream of dry ammonia gas, that hydrochloric acid gas, hydrogen, and vapours of ammonium chloride were evolved at the mouth of the tube (owing to the decomposition of the ferric chloride) and the iron thus liberated was partially united with nitrogen, forming a substance possessing a metallic lustre. It was found that this substance could not be so readily formed on passing the vapours of ammonium chloride through a tube similarly filled, on account of the difficulty experienced in regulating the temperature. If the temperature be not high enough, the ammonium chloride is not split up into ammonia gas and hydrochloric acid gas: consequently these gases cannot react upon the lava. Should the temperature rise by chance above a certain point, the nitride of iron is only formed with extreme difficulty, or that which has already formed is decomposed.

The above experiments were made by the author in 1870, and Tschermak published a short notice of them (*Min. Mitth.*, 1872, 1, 54).

Silvestri often noticed on fresh lavas a light grey and almost silver-white deposit, having a metallic lustre, and desired to ascertain whether it was identical with his artificially prepared iron nitride. Sartorius v. Waltershausen had also observed the same deposit upon some blocks of lava ejected from Etna in 1869, and carried the specimens he obtained to the author for examination, but they had already decomposed, owing doubtless to the action of acid vapours and solutions. This rapid decomposition is also observed with artificially prepared iron nitride. A specimen obtained from the lava of 1874 had a specific gravity of 3·147, was magnetic, and decomposed at a red-heat into free nitrogen, vapour of water, and magnetic oxide of iron. It was slowly attacked by acids, a fact which coincides with the author's observations of the artificial compound.

On fusing it with sulphur, sulphide of iron forms and nitrogen is evolved. Fremy (*Compt. rend.*, lii, 321) assigns the formula $Fe_5N_2$, Stahlschmid (*Pogg. Ann.*, cxxv, 37) $Fe_4N_2$, and Ragstadius (*Journ. f. prakt. Chem.*, 86) $Fe_6N_2$, to the artificial compound. On heating the natural substance in a stream of hydrogen, it was changed into metallic iron and ammonia, the amounts of which were estimated and found to be in 100 parts:

| | |
|---|---|
| Metallic Iron | 90·86 |
| Nitrogen | 9·14 |
| | 100·00 |

from which is deduced the same formula as that given by Fremy to the artificial compound. The author considers it very probable that this iron nitride has played a very important part in volcanic processes, as it appears that the metallic-shining compound is peculiar to blocks of lava possessing sharp edges found in the neighbourhood of craters, and in the middle of lava streams.

Lava may possess the property of absorbing nitrogen under certain conditions of temperature, and thus give rise to the formation of ammonium chloride, which is found so largely as a product of the fumaroles in crevices and holes. The decomposition of this ammonium chloride in presence of ferruginous lava may explain the presence of hydrogen amongst the products of volcanic action. The author proposes to name the natural iron nitride "Siderazote."

C. A. B.

## Double-refracting Garnets. By Arthur Wichmann (Pogg. Ann., clvii, 282—290).

It is well known that several minerals crystallising in the regular system exhibit certain optical irregularities, the best known of this class being boracite, analcime, diamond, and senarmontite. Des Cloiseaux described some peculiar optical properties observed on a crystal of grossular (garnet) in 1867 (*Nouvelles récherches sur les propriétés optiques des Cristaux*, &c. Paris, 1867, p. 8). He says, "the green

crystals from Wilsui exhibit in parallel polarized light, a 'marqueterie' composed of a large number of variously coloured parts, all of which disappeared in the same azimuth. In converging light, certain spots exhibit a large black band which sometimes increases to a curve somewhat resembling the hyperbola of a system of rings of a double-refracting biaxial substance." Des Cloiseaux did not make any further experiments to solve the problem of this extraordinary phenomenon. The author examined a thin section of a rhombic dodecahedron of grossular, in a Norremberg's polarizing apparatus, but failed to observe any of the above-mentioned phenomena, as the substance was completely isotropic. A microscopical examination of the same section showed that its substance was not homogeneous, as it contained various bodies possessing strong polarizing properties, but whose mineralogical nature could not then be determined. The garnet mass exhibited "polarization colours," with crossed Nichol's prisms on the spots which had a shell-like structure, the laminæ appearing alternately light blue or a dark greyish-blue. Where zones were absent the mass appeared completely dark. These observations prove that the "polarization colours" observed on grossular crystals arise from lamellar polarization. A microscopical examination of massive garnet (allochroite) was made, and the results divided into two classes, A and B.

A. The mass of the garnet does not consist of single individuals.

B. The mass consists of single individuals, subdivided into—

$\alpha$. The mass is built up of irregularly formed grains.

$\beta$. The mass is built up of well developed crystals.

The massive garnets from Wierum, near Drammen in Norway, from the Pfitschthal in the Tyrol, and from Beyreuth, are also isotropic, but that from Wurlitz, near Hof, is an exception, as it appears to be an aggregate of irregular grains when viewed in polarized light. These grains seem to be partially twinned and possess a dull bluish-grey colour; in diffused light, however, the mass does not appear to contain distinct individuals, a fact which is never observed with the massive garnets belonging to class B, $\alpha$: therefore the Wurlitz specimen may be a vesuvianite. The author examined some fine crystals from Berggiesshübel and Teufelstein, near Schwartzenberg, which exhibited a very distinct shell-like structure; it was also evident that these shells consisted of the same substance as the kernel itself. In polarized light the innermost crystal-kernel appeared quite dark, whilst the adjacent lamellæ were distinguished by the most brilliant colours. As proof that the shell-like structure is composed of the same substance as the garnet crystal itself, Wichmann gives the following instances:—

(1.) The irregularly developed grains also possess a similar shell-like structure to the others, and whilst the garnet-kernel appears quite dark in polarized light, the lamellæ appear alternately blue and yellow. (2.) A garnet crystal had endeavoured to develop itself, but attained only a rudimentary stage; it possessed a shell-like structure where there was a distinct interfacial angle, and the same phenomena were observed with this specimen in polarized light as in the examples given above. It is extremely difficult to assign a sufficiently clear cause for these phenomena. Each succeeding lamella on a crystal

individual should exhibit the same colours as the preceeding one. In polarized light this is not found to be the case, as three or four are sometimes alike *alternately*, but never *consecutively*.

The garnet-kernel was generally found to be simply refracting, one exception being a thin section of a garnet from Berggiesshübel, which exhibited scarcely any shell-like structure, whilst under the microscope in polarized light, the crystal appeared to be divided into six fields, the parallel fields possessing the same colour. As it was observed by Volger (*Pogg. Ann.*, 1854, xcii, 5—77) that the double-refracting power of boracite was occasioned by the presence of an aggregate of colourless crystals (parasite) passing through it, and gradually changing its composition, a similar decomposition may account for the phenomena observed with garnet, as the specimens examined were decomposed, the resulting product probably produces the phenomena. The author states that Breithaupt (*Handbuch. der Min.*, 1847, iii, 653) was right in classing typical colophonite with idocrase (vesuvianite), as it does not exhibit any enclosures and is double refracting, besides differing in colour from massive garnet. The so-called common colophonite from Escurial and Breitenbrunn is undoubtedly "massive" and "granular" garnet, whilst the typical colophonite is certainly vesuvianite.

C. A. B.

## On the existence of Microline, a new species of Triclinic Felspar with Potash Base, its Optic and Crystallographic Properties, and Chemical Composition. By A. Des Cloizeaux (Compt. rend., lxxxii, 885).

A species of felspar, generally considered as orthoclase, and apparently dimorphous with it, but referred to the triclinic system by reason of its optic properties. Chemically its base is essentially potash, the proportion of soda found being in proportion to the inclusions of albite, which are visible with the microscope. This is shown by the following analyses taken from a series, A being a pure specimen from Magnet Cove; B an arragonite from Murinsk, with rare inclusions of albite; C a clear green variety, irregularly spangled with hexagonal plates of oligiste, with broad bands of albite—

| | $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$ | KHO. | NaHo. | Loss on ignition. | Total. | Density. |
|---|---|---|---|---|---|---|---|---|
| A .... | 64·30 | 19·70 | 0·74 | 15·60 | 0·48 | 0·35 | 101·17 | 2·54 |
| B .... | 65·55 | 20·30 | — | 13·90 | 1·66 | — | 101·41 | 2·56 |
| C .... | 64·90 | 20·92 | 0·28 | 10·95 | 3·95 | 0·20 | 101·20 | 2·57 |

C. H. P.

## Daubreite (Oxychloride of Bismuth), a new Mineral. By J. Domeyko (Compt. rend., lxxxii, 922).

The specimens were obtained from Cerro de Tazna, from the bismuth mine of Constancia in Bolivia, where they occur in tolerable abundance. The mineral forms an earthy mass of yellowish or greyish colour, containing a large quantity of opaque crystalline plates of

pearly lustre, which give it sometimes almost a fibrous texture. Hardness 2 to 2·5; density 6·4 to 6·5. An analysis showed it to consist of oxychloride of bismuth, mixed with a mere trace of ferric oxide, in the proportions indicated by the formula $4Bi_2O_3.BiCl_3$. It is therefore intermediate between the two oxychlorides already known, which have been artificially prepared.

C. H. P.

## Quantities of Nitrates and of Ammonia in the Water of the Seine taken on the 18th of March, 1876. By J. B. Boussingault (Compt. rend., lxxxii, 658).

The water contained per litre—

Ammonia 0·00033 grm.
Nitric acid 0·00120 grm. = ·0022 $KNO_3$.
Suspended matter 0·210 grm.

In 1857 Seine water taken at the same place contained per litre—

Ammonia 0·00012 grm.
Nitric acid 0·0056 grm. = 0·0105 $KNO_3$.

By way of comparison 1 litre of Rhine water taken at Lauterbourg contained—

Ammonia 0·0002 to 0·0005 grm. } in the years
Nitric acid 0·0011 grm. = ·002 $KNO_3$ } 1857—1858.

C. H. P.

## Composition of Atmospheric Air at different Heights. By L. Mendelejeff (Bull. Soc. Chim. [2], xxv, 394).

The correctness of the application of Dalton's law to the determination of the composition of the different beds or strata of the atmosphere is stated by the author to be confirmed by the analyses of samples of air taken from the summits of mountains in America by Boussingault, and also of samples obtained by Miller when in a balloon. Gay-Lussac's results are probably incorrect. The differences in the amounts of oxygen contained in the air, calculated by the hypsometric formula, exceed those observed by actual analysis. The author considers that the existence of rising currents may account for this, as these currents are not produced by the effect of heat alone, but also by the varying amounts of vapour contained in the different strata of the atmosphere; it therefore follows from Dalton's law that the vapours present in lower strata can rise into the upper strata.

C. A. B.

# Organic Chemistry.

**Researches on Transpositions of Atoms.** By V. MEYER and F. FORSTER (Deut. Chem. Ges. Ber., ix, 529—544).

WHEN an iodide of an alcohol-radicle is heated with silver nitrite, a nitro-compound and a nitrous ether are simultaneously formed, with the exception of methyl iodide, which yields only nitromethane. To explain this, Tscherniak assumes that the nitro-compound is a primary product and the nitrous ether a secondary one, which is thus produced: a part of the oxide is resolved into an olefine and hydriodic acid, which latter acts on the silver nitrite, and the nitrous acid thus set free combines with the olefine in the nascent state.

To test the correctness of this view, the authors have examined the nitrites of primary and secondary propyl which are formed in the preparation of the corresponding nitro-compounds, because in this case the nitrites must be identical if the above hypothesis is correct.

The primary propyl nitrite, after being separated as much as possible from the nitropropane by distillation, was added slowly to a mixture of tin and hydrochloric acid. Thus the nitro-compound was converted into propylamine hydrochloride, and the nitrite into the alcohol, which was distilled off and purified. It was pure *primary* propyl alcohol without a trace of the secondary compound. The secondary iodide treated in the same way yielded pure *secondary* propyl alcohol, showing that Tscherniak's explanation is not the right one.

When isopropylamine is converted into the alcohol by Linnemann's reaction, only a small yield of the secondary alcohol is obtained, and the nitrogen which escapes contains a gas which seems to be propylene.

According to Linnemann and Siersch, the normal propylamine is by the same reaction converted into the secondary alcohol, but this is only a secondary product; at the same time a large quantity of the primary is formed, which was converted into propionic acid and propylnitrolic acid. The nitrogen which escapes contains propylene, and the formation of this explains that of the secondary alcohol, which is produced by the olefine combining in the nascent state with water. The decomposition of propylamine nitrite is therefore explained by the following equations:—

$$CH_3—CH_2—CH_2—NH_2.NO_2H = CH_3—CH_2—CH_2.OH + N_2 + H_2O.$$

$$CH_3—CH_2—CH_2.NH_2.NO_2H = CH_3—CH{=}CH_2 + N_2 + 2H_2O.$$

$$CH_3—CH{=}CH_2 + HOH = CH_3—CH(OH)CH_3.$$

C. S.

**Composition of Coal Gas.** By M. BERTHELOT (Compt. rend., lxxxii, 871—875 and 927—932).

THE author describes a method of determining the amount of benzene vapour in a volume of coal gas which need not exceed 15 c.c. The gas, deprived of carbonic acid, is collected over water in a vessel which is closed, when full, by a cork supporting a tube of about 1 c.c. capacity, filled with fuming nitric acid. On agitating the apparatus, the benzene is quickly converted into nitro-benzene, and after the nitric vapours have been absorbed by a little potash, the volume of residual gas is ascertained by transferring it to a graduated vessel, the initial volume having been previously determined by a careful gauging of the apparatus under like conditions. In the Paris gas the author in this way found benzene vapour to the amount of 3 to 3·5 volumes per hundred. Experiments by other methods furnished confirmatory figures, and careful examination of the products obtained by the action of sulphuric acid on the gas, enabled the author to assign the following figures as representing the quantities of the respective substances present in 1,000,000 volumes of the illuminating gas experimented upon:—

| | | |
|---|---|---|
| Vapour of benzene | $C_6H_6$ | 30000 to 35000 |
| Acetylene | $C_2H_2$ | 1000 |
| Ethylene | $C_2H_4$ | 1000 to 2000 |
| Propylene | $C_3H_6$ | 2·5 |
| Allylene | $C_3H_4$ | 8 |
| Butylene, &c. | $C_4H_8$ | traces |
| Crotonylene | $C_4H_6$ | 31 |
| Terpene | $C_{10}H_{16}$ | 42 |
| Other hydrocarbons | | 98 |

The author has found that at a red-heat acetylene and ethylene unite to form ethylacetylene, and he has also discovered that acetylene and propylene, under the same conditions, directly combine to constitute propylacetylene, an extremely volatile liquid, easily acted upon by sulphuric acid. He believes that at a red-heat the original constituents of coal undergo preliminary analytical actions, the ultimate products of which would be the four hydrocarbons: acetylene, ethylene, methane, and ethane, and polymerides of the first two, viz., $nC_2H_2$ and $nC_2H_4$, but that they immediately react upon each other, so as to produce synthetically, in accordance with regular laws of chemical equilibrium, the whole system of hydrocarbons to which destructive distillation gives rise; *e.g.*, cinnamene, $C_8H_8$, from acetylene and benzene; naphthalene, $C_{10}H_8$, from acetylene and cinnamene; acenaphthene, $C_{12}H_{10}$, from acetylene and naphthalene; anthracene, $C_{14}H_{10}$, from cinnamene and benzene; all these hydrocarbons being found in coal-tar.

R. R.

## Formation of Aldehyde from Derivatives of Benzene.

By E. ERLENMEYER (Deut. Chem. Ges. Ber., ix, 273).

WHEN salicylic or metoxybenzoic acid is oxidised by chromic acid *acetic acid* is formed, and metasulphocinnamic and metasulphophenylpropionic acid yield aldehyde and acetic acid.

C. S.

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## Cyano-cyanate of Chloral. By C. O. CECH (Compt. rend., lxxxii, 989—990).

WHEN equivalent quantities of hydrate of chloral, potassium cyanate, and potassium cyanide are mixed in dilute solutions, a violent action takes place, with disengagement of hydrocyanic acid, and an oil is produced which soon solidifies into acicular crystals. These are soluble in ether, alcohol, glacial acetic acid, sulphide of carbon, and water; they melt at 80°. Analysis shows that this substance would agree with a compound of chloral, hydrocyanic acid, and cyanic acid—

$$C_2HCl_3O + CNH + CNOH = C_4H_3Cl_3N_2O_2,$$

and the products of its decomposition confirm this view. This is the first known instance in which hydrocyanic and cyanic acids have been shown to possess the property of forming addition-products with an aldehyde.

R. R.

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## Action of Allyl-iodide on Potassium Sulphocyanate.

By O. BILLETER (Deut Chem. Ges. Ber., viii, 820).

AGAINST the usual supposition that allyl iodide treated with potassium sulphocyanate does not yield allyl-sulphocyanate, Billeter finds, in accordance with Gerlich (this Journal, 1875, p. 1029) that, after separating the sulphocarbimide with ammonia, a considerable quantity of allyl sulphocyanate remains, which exhibits properties identical with that prepared synthetically by him.

W. R.

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## Ethyl- and Methyloxamethane. By O. WALLACH and P. WEST (Deut. Chem. Ges. Ber., ix, 262—266).

*Ethylphenyloxamide*, $C_2O_2\left\{\begin{matrix}NH(C_2H_5)\\NH(C_6H_5)\end{matrix}\right.$, is obtained by the action of aniline on ethyloxamethane; it dissolves but sparingly in water, and crystallises from alcohol in white, glistening needles, melting at 169°.

*Methylethyloxamide*, $C_2O_2\left\{\begin{matrix}NH(C_2H_5)\\NH(CH_3)\end{matrix}\right.$, is formed by treating ethyloxamethane with methylamine. It dissolves in hot water, and separates from alcohol in crystals melting at 155°—157°. Phosphorus pentachloride acts on it as on its analogues, yielding *chloroxalmethylethyline*, $C_5H_7ClN_2$, an oily liquid boiling at 212°—213°. The *hydrochloride*, $C_5H_7ClN_2.ClH$, is a very hygroscopic and crystalline salt;

the *platino-chloride* crystallises in large thick plates. The methiodide, $C_5H_7ClN_2,ICH_3$, is readily soluble in water and a stable body. The argento-nitrate, $C_5H_7ClN_2,NO_3Ag$ forms transparent prisms.

When phosphorus pentachloride is added to a solution of ethyl-oxamethane in petroleum-naphtha, the following reaction takes place:—

$$C_2O_2\left\{\begin{matrix}NH(C_2H_5)\\CO_2C_2H_5\end{matrix}\right. + PCl_5 = C_2OCl_2\left\{\begin{matrix}NH(C_2H_5)\\CO_2 . C_2H_5\end{matrix}\right. + POCl_3.$$

On cooling by a freezing mixture, the dichloride crystallises out in large transparent prisms.

*Methyloxamethane*, $CO_2O_2\left\{\begin{matrix}NH(CH_3)\\CO_2C_2H_5\end{matrix}\right.$, is formed by passing methylamine into oxalic ether; it is an oily liquid, which is soluble in water and solidifies below 0°. By treating it with ammonia or amines, the following compounds were obtained:—

*Monomethyloxamide*, $C_2O_2\left\{\begin{matrix}NH(CH_3)\\NH_2\end{matrix}\right.$, forms microscopic needles, dissolving sparingly in water and alcohol, and melting at about 227°—229°. *Phenylmethyloxamide* crystallises in thin white needles, and melts at 171°—173°. *Methylethyloxamide* is identical with the compound already described. *Dimethyloxamide* separates from hot water in crystals melting at 209°—210°, and is identical with the product obtained by treating oxalic ether with aqueous methylamine. When ethylmethyloxamate is shaken with an alkali, salts of Wurtz's methyloxamic acid are formed; the free acid forms thin white needles, and the calcium-salt either anhydrous needles resembling asbestos, or large prisms containing water.

C. S.

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## Dinitro-compounds of the Fatty Group. By E. TER MEER (Liebig's Annalen, clxxxi, 1—22).

WHEN bromine is added to a cold dilute solution of ethylnitrolic acid, a heavy oil separates out, which is partially decomposed by distillation. On shaking with concentrated potash, crystals of potassium-dinitroethane and potassium bromide separate out, while an oil is left, which is violently acted upon by alcoholic potash, with formation of the same compounds as above. These facts show that by the action of bromine on ethylnitrolic acid, two bromine-compounds are formed, one which is decomposed by aqueous potash, and which is most probably *bromodinitroethane*—

$$CH_3C(NOH)NO_2 + 2Br_2 + H_2O = CH_3 . CBr(NO_2)_2 + 3HBr,$$

while the second is *dibromonitroethane*, which alcoholic potash easily converts into the dinitro-compound, with partial destruction of the dibromide; this, however, may be avoided by adding potassium nitrite:

$$CH_3.CBr_2NO_2 + 2KOH + KNO_2 = CH_3.CK(NO_2)_2 + 2KBr + H_2O + O.$$

As, according to this equation, oxygen is set free (which, of course, oxidises the alcohol), monobromnitroethane was treated in the same way, and thus pure potassium-dinitroethane was obtained—

$$CH_3.CHBr(NO_2) + KOH + KNO_2 = CH_3CK(NO_2)_2 + KBr + H_2O.$$

On decomposing the potassium-salt with dilute sulphuric acid, dinitroethane is obtained, a colourless, very refractive liquid, which is sparingly soluble in water, freely in alcohol and ether, and has a faint vinous smell and a peculiar sweet taste. It boils at 185°—186° (corrected), easily volatilises with steam, and has, at 23·5°, the spec. grav. 1·3503. Dinitroethane is a strong acid, reddening litmus and slowly decomposing carbonates.

*Potassium dinitroethane* forms yellow, glistening, monoclinic crystals, being combinations of $\infty P$, $\infty P\infty$, $0P$ and $P\infty$; $a : b : c = 0·58124 : 1 : 99016$. It is as explosive as potassium picrate, dissolves sparingly in cold, freely in hot water, with a deep yellow colour. In absolute alcohol and ether it is insoluble.

The sodium and ammonium salts are very similar compounds. The barium- and calcium-salts crystallise in small yellow needles or plates. Solutions of the salts give the following reactions:—

| | | | |
|---|---|---|---|
| Ferric chloride ..... | gives a | reddish-brown | precipitate. |
| Normal lead acetate .. | ,, | yellow crystalline | ,, |
| Basic lead acetate.... | ,, | voluminous yellow | ,, |
| Copper sulphate .... | ,, | light blue | ,, |
| Mercuric chloride .... | ,, | light brown | ,, |
| Mercurous nitrate .... | ,, | greyish-black | ,, |

The latter precipitate soon changes into colourless needles.

*Silver dinitroethane* is a yellow precipitate crystallising from hot water in small yellow and very brilliant plates.

When dinitroethane is treated with hydrochloric acid and tin, it yields acetic acid and hydroxylamine (compare this vol., page 67).

Sodium-amalgam and water reduce dinitroethane to a yellow, crystalline explosive body, which is, perhaps, azoxyethane, $CH_3.CHN_2O$.

Bromine acts readily on the potassium-compound, and produces *bromodinitroethane*, a colourless, heavy oil, having a very irritating smell; it decomposes on heating, and remains liquid at −17°. Alcoholic potash, and even aqueous alkalis, decompose it as follows:—

$$CH_3 . CBr(NO_2)_2 + 2KOH = CH_3CK(NO_2)_2 + KBr + H_2O + O.$$

When dinitroethane is heated with a mixture of sulphuric acid and nitric acid, the greater part is destroyed, and only a small quantity of crystals is formed, consisting, probably, of trinitroethane.

By the action of alcoholic potash and potassium nitrite on bromonitropropane, the potassium-compound of *dinitropropane* is easily obtained. It forms very explosive crystals, resembling potassium picrate. The free acid is an oil having the specific gravity 1·258 at 22·5°, and tasting and smelling like dinitroethane. It does not solidify

at $-17°$, and boils at 189°. In its reactions and its salts it shows the greatest analogy to the ethane-compound.

C. S.

**Propylene- and Isopropylene-guanamine.** By M. NENCKI (Deut. Chem. Ges. Ber., ix, 228—232).

THE author showed in a former paper (*Chem. Soc. J.*, 1875, 754), that guanidine formate and acetate split up on heating according to the equations—

$$(CN_3H_5CHOOH)_3 = C_3N_5H_5 + 4NH_3 + 2H_2O + 2CO + CO_2,$$
$$(CN_3H_5C_2H_4O_2)_3 = C_4N_5H_7 + 2(C_2H_4O_2NH_3) + CO_2 + 2NH_3.$$

In the former case, two molecules of formic acid split up directly into water and carbon dioxide, while a third is decomposed into $CO_2$ and $H_2$ because the two hydrogen-atoms are necessary for the complete conversion of the amido-group into ammonia. In the second case, two molecules of acid are eliminated unchanged as ammonia-salt, and the third is decomposed into $CO_2 + CH_2 + H_2$. The hydrogen-atoms convert two amido-groups into ammonia, while the methylene formed at the same time enters into the molecule of the new base, *acetoguanamine*. It seemed likely, therefore, that the other monobasic homologous fatty acids would, when heated with guanidine, furnish a series of basic bodies homologous with formo-guanamine and aceto-guanamine.

Guanidine butyrate was heated first, till strong fumes of ammonia were evolved; on treating the residue with caustic soda, a crystalline body with basic properties was obtained, for which the author proposes the name of *propylene-guanamine*. Its formation may be represented thus:—

$$(CN_3H_5.C_4H_8O_2)_3 = CH_3—CH_2—CH—C_3N_5H_5 + 2(C_4H_8O_2NH_3) + CO_2 + 2NH_3.$$

Propylene-guanamine forms anhydrous crystals when the aqueous solution is slowly cooled or evaporated on the water-bath; the crystals are four-sided rectangular plates, but when thrown down quickly from a hot solution, they are spherical or hemihedral forms (spheroïds), with curved faces. It is soluble in 53·7 parts of water at 14·5°, and in 7 parts of boiling water. Strong caustic soda precipitates it from an aqueous solution: ammonia from neither acid nor neutral solutions. It is easily soluble in alcohol. Heated in capillary tubes, it begins to sublime at 210°, and at 230° volatilises for the greater part without melting, and leaves a slight yellow residue. It dissolves in acids, and forms with them well crystallised salts, easily soluble in water and alcohol. The hydrochloride, $C_6H_{11}N_5HCl$, forms brilliant rhombic prisms and laminæ, and contains $1\frac{1}{2}$ molecules of water of crystallisation which it loses in air. An argentonitrate, which forms fine crystals, may be obtained by heating a concentrated aqueous solution with silver nitrate. Its formula is $C_6H_{11}N_5NO_3Ag$.

By employing isobutyric, instead of butyric acid, isopropylene-

guanamine is formed. It dissolves in 48·6 parts of boiling water, and in 176·7 parts of water at 18°. It is somewhat less soluble in alcohol than normal propylene-guanamine. It crystallises from aqueous solutions in pointed rhombohedrons resembling calcite, or in prisms with the two rhombohedrons aggregated in rows, as in quartz. It is distinguished from the normal base by being thrown down by ammonia from its solutions in strong mineral acids. Nitrate of isopropylene-guanamine, $C_6H_{11}N_5NO_3H$, crystallises in small tufts of concentric needles. The argentonitrate is more soluble in water than that of the normal base. It forms prismatic crystals.

G. T. A.

## Products of Decomposition of Aceto (Methylene-) Guanamine.

By M. Nencki (Deut. Chem. Ges. Ber., ix, 232—239).

Formoguanamine is either not attacked by acids and alkalis, or it is entirely decomposed by the continued action of oxidising agents, but acetoguanamine yields several products intermediate between itself and its final product, cyanuric acid.

*Guanide*, $C_4N_4H_6O$, is formed by the action of concentrated alkalis on aceto-guanamine—

$$C_4N_5H_7 + H_2O = C_4N_4H_6O + NH_3.$$

It is insoluble in water, alcohol, dilute acetic acid, and ammonia, but dissolves easily in mineral acids, and forms salts with them. It dissolves also in the fixed alkalis, and forms with their hydrates compounds which are soluble in water but not in alcohol. It therefore resembles guanine, which may be regarded as guanide in which a hydrogen-atom has been replaced by CN. The hydrochloride, $C_4N_4H_6OHCl$, crystallises in rhombic needles. The compound with potassium hydrate has the composition $(C_4N_4H_6OKOH)_2.1\frac{1}{2}H_2O$, that of the corresponding sodium salt being $C_4N_4H_6ONaOH.H_2O$. A solution of guanidine in nitric acid gives a crystalline precipitate with silver nitrate, consisting of $C_4N_4H_6OAgNO_3$.

*Guanamide*, $C_4N_3H_5O_2$. This body is obtained by heating one part of aceto-guanamine with two parts of concentrated sulphuric acid to 150°, and mixing the cooled liquid with absolute alcohol, which throws down a bulky precipitate. The decomposition takes place in accordance with the equation—

$$C_4N_5H_7 + 2H_2O = C_4N_3H_5O_2 + 2NH_3.$$

Guanamide is easily soluble in water, acids, and alkalis, but little so in alcohol, and crystallises from a hot alcoholic solution in small rhombic needles. A well crystallised platino-chloride,

$$(C_4N_3H_5O_2HCl)_2PtCl_4 + 4H_2O,$$

may be obtained in yellow tufts of concentric needles. When guanamide is dissolved in five to six times its weight of nitric acid (1·3 sp. gr.), a lively reaction takes place on warming, and cyanuric acid is formed, thus :—

$$C_4N_3H_5O_2 + 4O = C_3N_3H_3O_3 + CO_2 + H_2O.$$

A slow stream of chlorine passed into guanamide dissolved in a small amount of water causes the separation of a fine white crystalline body containing chlorine, and insoluble in cold water. This body may be crystallised from hot water, but the hot solution has a faint smell of chloroform. From its solution in dilute cold caustic soda it is precipitated for the most part unchanged by hydrochloric acid. When it is boiled for a long time with water, the chloroform smell becomes perceptible, and cyanuric acid can be detected in the solution. The decomposition is effected much more quickly on warming with alkalis. Nascent hydrogen produces the same decomposition. No chloroform could, however, be detected by the isonitril reaction. This body forms anhydrous crystals. It is perfectly decomposed at 140°. Its composition seems to be $C_4N_3Cl_2H_5O_3$. The action of chlorine on guanamide may be represented as—

$$C_4N_3H_5O_2 + 4Cl + H_2O = C_4N_3Cl_2H_5O_3 + 2HCl,$$

and its decomposition by alkalis as—

$$C_4N_3Cl_2H_5O_3 = C_3N_3O_3H_3 + CH_2Cl_2.$$

The author names this body *Dichloroguanamidine.*

The bromine-compound of guanamide is insoluble in hot and cold water, alcohol, and ether, and when boiled with water is decomposed into bromoform and cyanuric acid. Its probable composition is $C_4N_3Br_3O_3H_4$.

Its origin from guanamide is analogous to that of dichloroguanamidine, except that one more atom of hydrogen is replaced by bromine. It might be named tribromoguanamidine.

*Dichloroguanamine.*—When chlorine is passed into aceto-guanamine, dissolved in little water, a precipitate is finally obtained consisting of $C_4N_5H_5Cl_2$.

This body is insoluble in water, but easily soluble in alkalis, from which it is precipitated (with partial decomposition) by hydrochloric and acetic acids. When warmed with dilute hydrochloric acid it dissolves, while streams of chlorine escape, and from the solution soda or ammonia throws down a heavy soluble crystalline body which, when ammonia is the precipitant, looks very much like sal-ammoniac. This precipitate possesses faint basic properties, but on evaporation separates unchanged from a solution in oxalic acid. Its composition is $C_4N_5H_5Cl_2$. A platinum salt was obtained answering to the formula

$$(C_4H_5Cl_2N_5)_2.2HCl.PtCl_4;$$

and an argentonitrate, $C_4N_5H_5Cl_2.NO_3Ag$. This body affords a good case of isomerism, or, more probably, of polymerism. The original product of the action of chlorine on guanamine possesses decided acid properties, and passes by the action of acids into a basic body of similar composition, which must be considered as guanamine in which the two hydrogen atoms of the methylene have been replaced by chlorine.

There is a great analogy between the decomposition of aceto-guanamine and of melamine by acids and alkalis, thus :—

Boiled with alkali—

$$\underset{\text{Melamine.}}{C_3N_6H_6} + H_2O = \underset{\text{Ammeline.}}{C_3N_5H_5O} + NH_3.$$

$$\underset{\text{Acetoguanamine.}}{C_4N_5H_7} + H_2O = \underset{\text{Guanide.}}{C_4N_4H_6O} + NH_3.$$

Warmed with sulphuric acid—

$$\underset{\text{Melamine.}}{C_3N_6H_6} + 2H_2O = \underset{\text{Ammelide.}}{C_3N_4H_4O_2} + 2NH_3.$$

$$\underset{\text{Acetoguanamine.}}{C_4N_5H_7} + 2H_2O = \underset{\text{Guanamide.}}{C_4N_3H_5O_2} + 2NH_3.$$

By further oxidation—

$$\underset{\text{Melamine.}}{C_3N_6H_6} + 3H_2O = \underset{\text{Cyanuric acid.}}{C_3N_3H_3O_3} + 3NH_3.$$

$$\underset{\text{Guanamide.}}{C_4N_3H_5O_2} + 4O = \underset{\text{Cyanuric acid.}}{C_3N_3H_3O_3} + CO_2 + H_2O.$$

G. T. A.

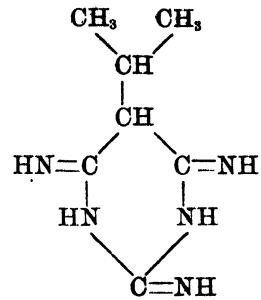
**The Condensation-products of Guanidine Valerate and Caproate.** By E. BAUDROWSKI (Deut. Chem. Ges. Ber., iv, 240—244).

THE action of heat on guanidine formate and acetate has been described, and this paper contains an account of the extension of the investigation to the higher members of the fatty acid series.

*Butylene Guanamine.*—The method of preparation was the same as before. The valeric acid used was obtained from fermentation amyl-alcohol. The base when pure consists of brilliant white needles belonging to the rhombic system. It is not very soluble in cold water, but more easily so in hot, and very easily in alcohol and ether. The melting point lies between 172°—173° (uncorrected), and the point of solidification at 127°. It partly sublimes at 100°. The crystals are anhydrous. The formula of the body is $C_7H_{13}N_5$, and its formation takes place according to the equation—

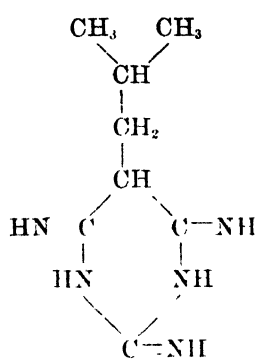
$$(CN_3H_5 \,.\, C_5H_{10}O_2)_3 = C_7H_{13}N_5 + 2(C_5H_{10}O_2 \,.\, NH_3) + CO_2 + 2NH_3.$$

The basic property of this body is weak. The acetic acid compound undergoes decomposition in the air. The hydrochloride and sulphate and the double salt with silver have been prepared. Butylene-guanamine is strictly analogous in its behaviour to methylene-guanamine, but differs in giving off a strong offensive odour when the product of oxidation is mixed with caustic soda, showing, undoubtedly, the presence of an isonitril—probably butylisonitril. The constitution of this new base may be expressed thus:



By displacement of a hydrogen atom by bromine in butylene-guanamide, $C_7H_{11}N_3O_2$, and replacement of the bromine by CN, a body can be obtained which is probably isomeric with theine.

*Amylene-guanamine*. $C_8H_{15}N_5$.—The hydrochloride was prepared. It forms white crystals of mother-of-pearl lustre, and is one of the finest of the guanamine salts. It is very easily soluble in water. Amylene guanamine itself consists of small microscopic crystals which are anhydrous, difficultly soluble in water, easily in alcohol. Its melting point lies between 177°—178° (uncorrected). Point of solidification about 144°. Its formula is:



G. T. A.

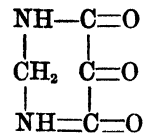
**On the Constitution of the Guanamines and the Polymeric Cyanogen Compounds.** By M. NENCKI (Deut. Chem. Ges. Ber., ix, 244—250).

THE guanidine salts of the monobasic fatty acids give rise on heating to a homologous series of guanamine bases in a way which may be expressed by the general equation—

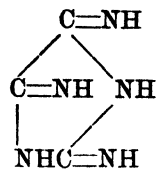
$$(C_nH_{2n}O_2CN_3H_5)_3 = C_{n+2}H_{2n+3}N_5 + 2(C_nH_{2n}O_2) + CO_2 + 4NH_3.$$

The constant occurrence of cyanuric acid as the last product of oxidation of the guanamines shows that the carbon-affinities set free on the condensation of guanidine, in consequence of the removal of amido-

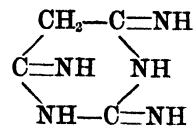
groups, do not become reciprocally linked, otherwise aceto-guanamine on continued oxidation would yield substituted ureas. In fact it was expected that by replacement of another NH residue by O a body would be obtained isomeric with barbituric acid, and of a structure—



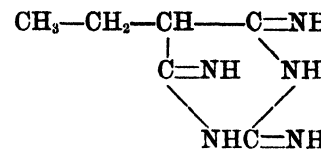
The formation of cyanuric acid by treating guanamide with nitric acid, and by boiling the chlorine and bromine derivatives of the latter with water, shows that in the guanamines the union of the three carbon-atoms of the guanadine takes place through the NH residue. The structure of these bases is therefore—



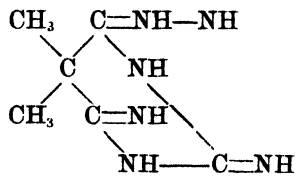
Formoguanamine



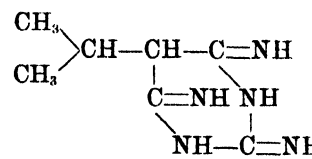
Aceto (methylene-) guanamine.



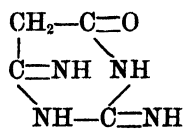
Propylene-guanamine.



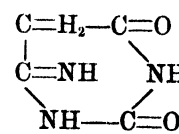
Isopropylene-guanamine.



Butylene-guanamine.

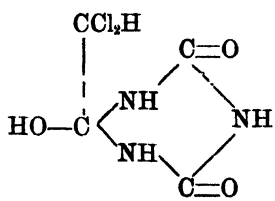


Guanide.

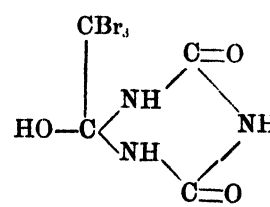


Guanamide.

The two derivatives formed by the action of chlorine and bromine on guanamide have probably the following structure:—

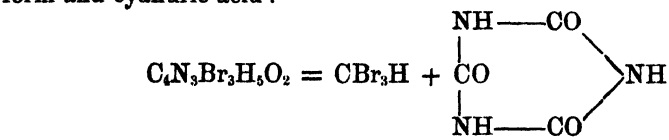


Dichloroguanamidine.

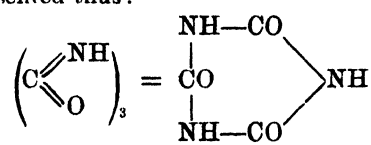


Tribromoguanamidine.

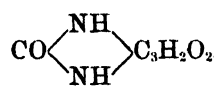
The closed chain is changed into an open one by the taking up of water, and a gentle heat then suffices to unloose the molecule: thus tribromo-guanamidine warmed with water is decomposed into bromoform and cyanuric acid :—



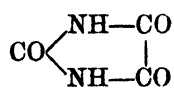
The structural formula thus found for cyanuric acid explains in the simplest way the relation of this body to cyanic acid, and the whole cyanogen-group. The passage of cyanic into cyanuric acid, and *vice versâ*, may be represented thus :—



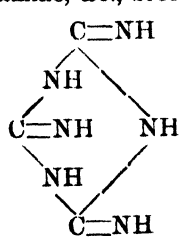
The hydrogen atoms of cyanuric acid which are replaceable by metals are those of the imido-groups, as in cyanic acid and the bibasic barbituric acid :—



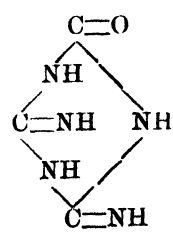
or parabanic acid.



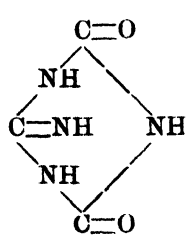
In accordance with the structure of the guamines and cyanuric acid, those of melamine, &c., become:—



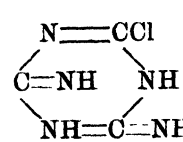
Melamine



Ammeline.

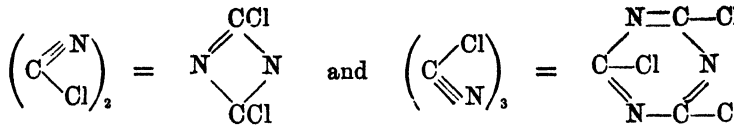


Melanuric acid.

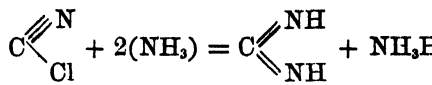


Chlorocyanamide.

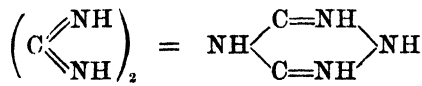
The change of gaseous chlorocyanogen into the liquid or solid may be represented as :—



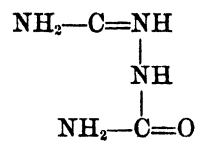
and also its conversion into cyanamide by ammonia :—



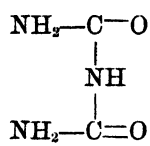
The change of cyanamide into dicyanamide is simple :—



The structural formula has already been applied by Mulder to dicyanamide. Dicyanamide takes up water and passes into dicyandiamidine, the structure of which is—



The closed chain of dicyanamide is opened by the addition of water, and dicyandiamidine corresponds with biuret, in which the diatomic NH residue replaces O :—

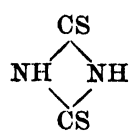


Biuret.

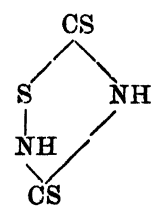
From this point of view the constitution of the sulpho-cyanogen compounds is simply explained. Persulphocyanic acid is decomposed by alcoholic potash into dithiocyanic acid and sulphur :—

$$C_2N_2S_3H_2 + 2KHO = C_2N_2S_2K_2 + S + 2H_2O,$$

and the structure of these bodies is as follows :—

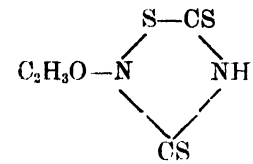


Dithiocyanic acid.

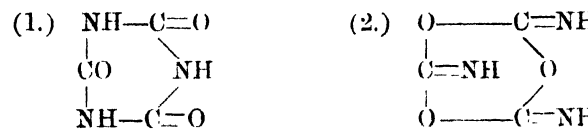


Persulphocyanic acid.

These formulæ also express very simply the behaviour of the persulpho-acid to reducing agents, as when it is reduced by nascent hydrogen to sulpho-urea. Acetylsulphocyanic acid :—

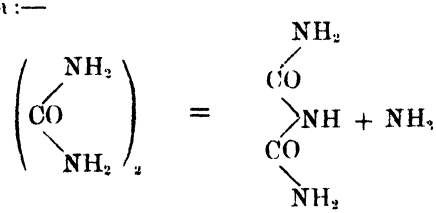


acted upon by nascent hydrogen in an acid solution also gives sulphourea. In this reaction the two imido-residues of the persulphocyanic acid are changed into amido-groups, with simultaneous separation of carbon sulphide. The formation of urea in this case shows that the sulphur or oxygen in the polymeric cyanogen compound is united by both affinities to the carbon, so that of the two possible formulæ for cyanuric acid—

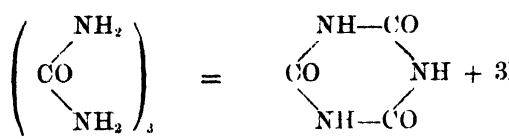


the first is the more probable.

The formation of the guanamines by heating the guanidine salts finds its perfect analogy in the formation of biuret and cyanuric acid by heating urea :—



and



In the first case two amido-groups give a diatomic NH residue with separation of ammonia : in the second case two amido-groups in each of the three urea molecules are converted into a NH residue and $NH_3$.

By further heating, ammelide and mellone are formed from urea, and although the (molecular) formulæ of these bodies are not known with certainty, yet from the equations of Laurent and Gerhardt—

$$4(CN_2H_4O) = \underset{\text{Ammelide.}}{C_3H_4N_4O_2} + CO_2 + NH_3,$$

$$6(C_3H_4N_4O_2) = 3(C_3H_3N_3O_3 + CHNO + NH_3) + \underset{\text{Mellone}}{C_6H_3N_9},$$

and the behaviour of these bodies to acids and alkalis, their molecular structure would seem to follow the same law of condensation, *i.e.*, the carbon atoms in the molecule are not linked by mutual bonds, but by those of the nitrogen.

G. T. A.

**Action of Benzoyl Chloride on Cyanamide and Sodium Cyamide.** By GUSTAVE GERLICH (J. pr. Chem. [2], xiii, 270—292).

DERIVATIVES of cyanamide containing metals or alcohol-radicles are well known, but all attempts to prepare and accurately investigate a cyanamide in which the hydrogen has been replaced by an acid radicle have been unsuccessful. The author endeavoured to prepare benzoyl-cyamide, in the expectation that it could be more easily obtained in the pure state than the corresponding acetyl compound. Though the attempt proved unsuccessful, some other interesting results were obtained, which are summed up in short as follows:—

(1.) Benzoyl chloride and cyanamide do not react on each other either in presence of ether or when heated by themselves, as was expected according to the equation—

$$3CyNH_2 + 2C_6H_5COCl = CyNH_2.2HCl + 2CyNHC_6H_5CO.$$

(2.) Benzoyl chloride and dry sodium cyamide give benzoyl-ammeline, benzonitril, carbon dioxide, and sodium chloride.

(3.) Benzoyl chloride and sodium cyamide in presence of ether give benzoyl-cyamide and sodium chloride.

(4.) Benzoyl-cyamide is decomposed as it is formed, and if in ethereal solution, separates partly into carbon dioxide, benzonitril, and cyanamide.

(5.) Benzoyl-cyamide becomes polymerised on longer digestion of its ethereal solution partly into tribenzoyl-melamine.

(6.) Benzoyl-ammeline breaks up on heating into carbon dioxide, cyanimide, and benzonitril.

(7.) Tribenzoyl-melamine gives, when heated in a stream of hydrogen, carbon dioxide, hydrocyanic acid, benzonitril, dibenzoyldicyanodiamide, and pseudo-triphenyl-melamine.

(8.) Benzoyl-cyamide mixed with sodium ethylate in ethereal solution gives sodium-benzoyl-cyamide.

(9.) Sodium-benzoyl-cyamide is decomposed on heating into benzonitril and sodium cyanate.

A comparison of the properties of cyanamide and its derivatives with those of uric acid shows that there are no grounds for regarding the latter as a derivative of cyanamide (as tartro-cyamide). While acting upon sulpho-urea at a low temperature with precipitated oxide of mercury perfectly free from alkalis, the author obtained a white crystalline body, which slowly turned grey, and finally black. Attempts to reproduce this body under the same conditions of temperature and absence of alkalis failed, but a specimen was accidentally obtained on a second occasion. The author believes that the body is mercury-urea, $NHgCSNH_2$.

G. T. A.

## Diphenyl and Diphenyline. By G. SCHULTZE (Deut. Chem. Ges. Ber., ix, 547—549).

A MODIFICATION of Berthelot's method of preparing diphenyl is recommended. In the upper end of an iron tube heated by a combustion furnace, the whole being placed slantingly, is fixed a separating funnel in place of a boiling-flask, from which the benzene is allowed to drop slowly; the other end is attached to a tubulated receiver on a water-bath, which is also connected with an upright condenser. By this arrangement the diphenyl is freed from acetylene and hydrogen. The yield is about 50—60 per cent. of the benzene employed, only a small amount of carbon being deposited.

If diphenyl be treated with fuming nitric acid diparanitro- and iso-dinitrodiphenyl are obtained; when the latter is reduced, an isomeride of benzidine, having this formula $C_{12}H_8\left\langle\begin{matrix}NH_2\\NH_2\end{matrix}\right.$, is formed. This the author proposes to call *diphenyline*. It dissolves with difficulty in cold water, easily in alcohol and ether, crystallising from alcohol in large shining plates, which melt at 53°. The sulphate, as well as other salts, are very insoluble in water. When the base is dissolved in large excess of hydrochloric acid, a substance, having the formula $C_{12}H_8(NH_2)_2.2HCl$, crystallises out in long needles. Diphenyline is easily oxidised, a brownish-black precipitate being formed on the addition of the oxidising agent. Another isomeride (m.p. 15°) has probably been obtained by fusing diamidophenanthrahydroquinone with sodium hydrate.

E. W. P.

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## Formation of Naphthalene from Turpentine-oil. By G. SCHULTZE (Deut. Chem. Ges. Ber., ix, 549).

WHEN oil of turpentine vapour is passed through a hot tube, carbon is deposited, hydrogen is evolved, and several hydrocarbons are formed, of which only naphthalene has been recognised; it melts at 80° and boils at 217°, forming with picric acid yellow needles melting at 149°.

E. W. P.

## Derivatives of Paratolylphenyl Ketone. By W. THÖRNER (Deut. Chem. Ges. Ber., ix, 482—485).

PARATOLYLPHENYL KETONE, $C_6H_5—CO—C_6H_4—CH_3$, when treated with chlorine, yields the following substitution-products:—

1. *Parabenzoyl-benzyl Chloride*, $C_6H_5—CO—C_6H_4—CH_2Cl$.—This body is formed by the action of chlorine on the ketone at 95°—110°. It crystallises in white prisms, which melt at 97°—98° and dissolve easily in chloroform, carbon bisulphide, toluene, and hot alcohol. It sublimes in large flat needles melting at 93°—94°.

2. *Parabenzoyl-benzylene Chloride*, $C_6H_5—CO—C_6H_4—CHCl_2$, is formed by the action of chlorine on the ketone at 120°—140°. It crystallises in large nacreous laminæ, melting at 94°—95°, and dissolves in the same liquids as the preceding compound. It is not

decomposed by boiling with water. Sublimes in large laminæ, melting at 85°·4—86°.

3. *Parabenzoyl-benzotrichloride*, $C_6H_5—CO—C_6H_4—CCl_3$, is obtained by the action of chlorine on the ketone at 150°—160°. It crystallises from glacial acetic acid in small silky laminæ melting at 107°—107·5°, and is easily soluble in benzene, ether and hot alcohol. When it is boiled with water the 3 atoms of chlorine gradually react with 2 mol. of water to form 3 mol. of hydrochloric acid, and Zincke's parabenzoyl-benzoic acid is produced. This decomposition takes place easily and completely at 180° in sealed tubes.

Paratolylphenyl ketone in alcoholic solution, when treated with zinc and hydrochloric acid, yields two isomeric products having the formula $C_{28}H_{24}O_2$, and termed provisionally α- and β-pinacolin.

The α-pinacolin is readily formed in almost theoretical proportion when a brisk evolution of hydrogen takes place in a very dilute solution of the ketone in 57 per cent. alcohol. It crystallises in white microscopic needles, which melt at 214°—215°.

The β-pinacolin is formed by the slow action of zinc and hydrochloric acid on the ketone in a quantity of absolute alcohol insufficient to dissolve it. It crystallises in highly refractive quadratic tables, which melt at 136°—137° and become turbid on drying.

Both the pinacolins dissolve easily in carbon bisulphide, chloroform, toluene, and hot acetic acid, and sparingly in hot alcohol and ether, but not in water. They are being further investigated.

J. R.

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**Formation of Vanillin from Eugenol.** By E. ERLENMEYER (Deut. Chem. Ges. Ber., ix, 273).

WHEN the potassium-compound of eugenol is oxidised with potassium permanganate, it yields vanillin and a polymeride of eugenol, which seems to be an intermediate product. C. S.

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**Arbutin.** By HLASIWETZ and HABERMANN (Chem. Centr., 1875, 276).

The authors find that this glucoside, when decomposed by acids or ferments, yields, together with sugar, not only hydroquinone, as generally supposed, but likewise methyl-hydroquinone. Moreover, from a revision of the published analyses of arbutin, they infer that its true formula is $C_{25}H_{34}O_{14}$. Adopting this formula, the decomposition above mentioned may be represented by the equation—

$$C_{25}H_{34}O_{14} + 2H_2O = C_6H_6O_2 + C_7H_8O_2 + 2C_6H_{12}O_6.$$

M. M. P. M.

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**Some Bromobenzenesulphonic Acids.** By W. LENZ (Liebig's Annalen, clxxxi, 23—47).

WHEN bromine is added slowly and in the cold to a solution of sulphanilic acid or its barium salt, *dibromamidobenzenesulphonic acid* is formed. Its barium salt is but sparingly soluble and easily decomposed by dilute sulphuric acid; the free acid thus obtained crystallises

in transparent obtuse prisms, which lose water of crystallisation in the air. On passing nitrous acid into its cold alcoholic solution, the diazo-compound, $C_6H_4Br_2\left\{\begin{matrix}N{=}N\\ SO_2\end{matrix}\right.$, separates out in microscopic, square, colourless or yellowish plates, which become darker in the air and have a bitter taste. On boiling it with absolute alcohol, it is converted into *dibromobenzenesulphonic acid*, forming a crystalline mass. The *ammonium-salt*, $C_6H_3Br_2SO_3NH_4$, forms glistening colourless scales. $C_6H_3Br_2SO_3K$ forms large brownish crystals. $(C_6H_3Br_2SO_3)_2Ba + 3\frac{1}{2}H_2O$ crystallises in long yellow needles. $(C_6H_3Br_2SO_3)_2Ca + 3\frac{1}{2}H_2O$ was obtained in small hexagonal plates. $(C_6H_3Br_2SO_3)_2Pb + 1\frac{1}{2}H_2O$ crystallises in white scales, consisting of microscopic needles. The *chloride*, $C_6H_3Br_2SO_2Cl$, is readily soluble in ether, sparingly in petroleum-naphtha, and separates from a mixture of the two in large transparent crystals melting at 57·5°. The *amide*, $C_6H_3Br_2SO_2NH_2$, crystallises from hot water in white scales, melting at 203°.

When the diazo-compound is heated with hydrobromic acid it is converted into *tribromobenzenesulphonic acid*, forming a yellow, crystalline, not hydroscopic, mass. $C_6H_2Br_3SO_3NH_4$ forms glistening, microscopic plates. $C_4H_2Br_3SO_3K$ crystallises in colourless plates. $(C_6H_2Br_3SO_3)_2Ba + 3H_2O$ is a white precipitate, crystallising from hot water in red, thin needles. $(C_6H_2Br_3SO_3)_2Ca + 2\frac{1}{2}H_2O$ is also but sparingly soluble, and crystallises from hot water in six-sided microscopic needles or in long needles. $(C_6H_2Br_3SO_3)_2Pb + 3\frac{1}{2}H_2O$ is a precipitate, crystallising from hot water in prisms. The *chloride*, $C_6H_2Br_3SO_2Cl$, forms four-sided prisms, and begins to soften at 123° and liquefies at 127°. The *amide*, $C_6H_2Br_3SO_2NH_2$, separates from hot water as a white crystalline powder, melting at 210°. *Nitrodibromobenzenesulphonic acid*, $C_6H_2Br_2(NO_2)SO_3H$, was obtained by the action of nitric acid on the barium salt of the dibromo-acid; it crystallises in plates containing water. $C_6H_2Br_2(NO_2)SO_3NH_4$ forms small thick crystals; on heating it with alcoholic ammonia to 230° half the bromine is removed and a compound is formed, which appears to be a bromonitroamidobenzenesulphonic acid. $C_6H_2Br_2(NO_2SO_3K + H_2O$ crystallises in glistening, brittle plates. $(C_6H_2Br_2(NO_2)SO_3)_2Ba + 1\frac{1}{2}H_2O$ is a precipitate, crystallising from hot water in rhombohedrons or in plates which contain 4 mol. of water. $(C_6H_2Br(NO_2)SO_3)Ca + 3H_2O$ is a crystalline powder. $(C_6H_2Br_2(NO_2)SO_3)_2Pb + 5H_2O$ is sparingly soluble, and crystallises from hot water in microscopic plates. $C_6H_2Br_2(NO_2)SO_2Cl$ forms colourless, transparent plates, which become soft at 118° and liquid at 121°. $C_6H_2Br_2(NO_2)SO_2NH_2$ is an indistinctly crystalline mass, which blackens at 300° without melting.

Tin and hydrochloric acid convert the nitro-acid but slowly into an *amidodibromobenzenesulphonic acid*, which forms a crystalline powder and is isomeric with dibromosulphanilic acid. $(C_6H_2Br_2(NH_2)SO_3)_2Ba + 3\frac{1}{2}H_2O$ is a precipitate crystallising from hot water in needles. $(C_6H_2Br_2(NH_2)SO_3)_2Ib,PbO,4H_2O$ is obtained as a precipitate by adding basic lead acetate to a solution of the acid; from hot water it separates as a sandy, crystalline powder. The diazo-compound,

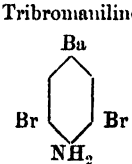
$C_6H_2Br_2\left\{\begin{matrix} N{=}N \\ \diagup \\ SO_2 \end{matrix}\right.$, crystallises in needles and explodes on heating, but not by percussion. Boiling absolute alcohol converts it into the dibromobenzene-sulphonic acid, described above, and by heating it with concentrated hydrocromic acid, it yields a *tribromobenzenesulphonic acid.* $C_6H_2Br_3SO_3K + H_2O$ is sparingly soluble in cold water, and crystallises from a hot solution in flat, silky needles. $(C_6H_2Br_3SO_2)_2Ba_2 + H_2O$ is a precipitate, crystallising from hot water in slender needles or small plates. The *chloride* $C_6H_2Br_3SO_2Cl$ forms large, transparent plates, melting at 86°.

By the action of nitric acid on the tribromobenzenesulphonic acid, which has previously been described, a *nitrotribromobenzenesulphonic acid* is formed, which is crystalline and hygroscopic. $C_6HBr_3(NO_2)SO_3NH_4 + H_2O$ forms small, flat needles. $C_6HBr_3(NO_2)SO_3K + H_2O$ crystallises from hot water in granules. $(C_6HBr_3(NO_2)SO_3)_2Ba + 4H_2O$ forms silky prisms. $(C_6HBr_3(NO_2)SO_3)_2Ca + 3H_2O$ forms microscopic crystals. $(C_6HBr_3(NO_2)SO_3)_2Pb + H_2O$ is a colourless, sparingly soluble powder. $C_6HBr_3(NO_2)SO_2Cl$ forms small crystals, melting at 116°. $C_4HBr_3(NO_2)SO_2NH_2$ is a white powder, melting at 202°. By reducing the nitro-acid it yields *amidotribromobenzenesulphonic acid*, crystallising in tufts of flexible needles. $(C_6HBr_3(NH_2)SO_3)Ba + 1\frac{1}{2}H_2O$ is a precipitate crystallising from hot water in microscopic plates. The diazo-compound is a white, crystalline powder, which boiling hydrobromic acid converts into *tetrabromobenzenesulphonic acid.* $C_6HBr_4SO_3K + H_2O$ is a crystalline precipitate, which crystallises from hot water in microscopic plates. $(C_6HBr_4SO_3)_2Ba + H_2O$ is also sparingly soluble in cold water and crystallises from a hot solution in transparent rhombic needles. $C_6HBr_4SO_2Cl$ crystallises in small, rhombic needles, melting at 120°; and $C_6HBr_4SO_2NH_2$ forms a crystalline powder, which melts at 181°.

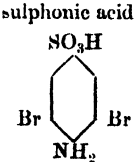
The starting point of the compounds described in this paper is sulphanilic acid, which is a para-compound, and when treated with an excess of bromine is converted into tribromaniline. The constitution of the different compounds, taken in the same succession as described, is therefore as follows:—

Sulphanilic.

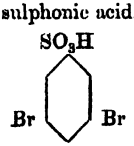
Tribromaniline.



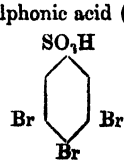

Dibromamidobenzene-sulphonic acid.



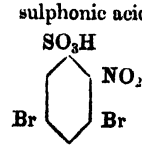

Dibromobenzene-sulphonic acid.



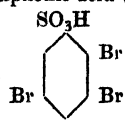

Tribromobenzene-sulphonic acid (1).



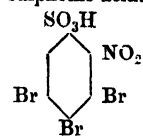

Nitrodibromobenzene-sulphonic acid.



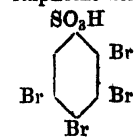
Tribromobenzene-sulphonic acid (2).




Nitrotribromobenzene-sulphonic acid.




Tetrabromobenzene-sulphonic acid.




C. S.

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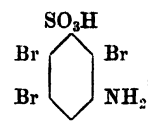
**Derivatives of Benzenesulphonic Acid.** By H. LIMPRICHT (Deut. Chem. Ges. Ber., ix, 474—480).

*Tribromometamidobenzenesulphonic acid,*

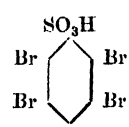



is easily obtained by mixing a hot aqueous solution of metamidobenzenesulphonic acid with 3 mol. of bromine. The diazo-compound of this acid separates as a yellow crystalline powder on passing nitrous anhydride into the strong alcoholic solution: when heated with absolute alcohol under pressure, it yields

*Tribromobenzenesulphonic acid*, $C_6H_2Br_3SO_3H$.—This acid forms salts which are, for the most part, sparingly soluble in water: they all contain water of crystallisation. The *chloride*, $C_6H_2Br_3SO_2Cl$, forms large prisms, melting at 64·5. The *amide*, $C_6H_2Br_3SO_2NH_2$, forms silky needles.

*Nitrotribromobenzenesulphonic acid*, $C_6H(NO_2)Br_3SO_3H.2H_2O$, obtained by boiling the preceding compound with strong nitric acid, forms white stellate groups of needles, easily soluble in hot water and alcohol. The *chloride*, $C_6H(NO_2)Br_3SO_2Cl$, forms flat tables melting at 142°. The *amide*, $C_6H(NO_2)Br_3SO_2NH_2$, crystallises in small needles melting at 175°.

*Tetrabromobenzenesulphonic acid*—




$+ 5H_2O$,

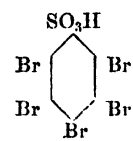
is obtained by heating the diazo-compound of tribromometamidobenzenesulphonic acid with hydrogen bromide. It forms white needles, which dissolve easily in water and alcohol. Its ammonium and potassium salts are anhydrous: the barium, calcium, lead, and silver salts crystallise with water. The *chloride*, $C_6HBr_4SO_2Cl$, forms thick rhombic tables melting at 91·5°. The *amide*, $C_6HBr_4SO_2NH_2$, forms microscopic needles melting above 250°.

*Nitrotetrabromobenzenesulphonic acid*, $C_6(NO_2)Br_4SO_3H,4H_2O$.—Obtained by boiling the preceding compound with strong nitric acid, forms yellowish-white shining needles soluble in alcohol and water.

Its ammonium, potassium, barium, calcium, lead, and silver salts crystallise with water. The *chloride*, $C_6(NO_2)Br_4SO_2Cl$, forms rhombic tables melting at 146°—147°. The *amide*, $C_6(NO_2)Br_4SO_2NH_2$, crystallises in microscopic needles melting above 300°.

*Amidotetrabromobenzenesulphonic acid*, $C_6(NH_2)Br_4SO_3H.2H_2O$, is obtained by heating the foregoing compound with tin and hydrochloric acid. It forms delicate needles, which dissolve easily in hot water and alcohol. Its aqueous solution gives no bromanil when treated with bromine or chromic acid. The potassium, barium, and calcium salts crystallise with water. The alcoholic solution of the acid, when nitrous acid is passed into it, deposits the diazo-compound in the form of a yellow powder, which, when decomposed with hot hydrobromic acid, yields—

*Pentabromobenzenesulphonic acid*,




This substance crystallises in needles and laminæ, which dissolve very slightly in water, and sublime, with decomposition, at 180°—220°. It is not affected by boiling with strong nitric acid or potash-ley. Its ammonium salt is anhydrous, the potassium, barium, calcium, and silver salts crystallise with water. The *chloride*, $C_6Br_5SO_2Cl$, forms warty masses of small needles melting at 90°. The *amide*, $C_6H_5SO_2NH_2$, is a crystalline powder blackening without melting at 250°.

J. R.

## On Sulphoparabromo- and Sulphometabromobenzoic Acids.

By C. Böttinger (Deut. Chem. Ges. Ber., ix, 177—182).

Contains nothing worth reproducing.

J. R.

## On Usnic Acid.

By E. Paternò (Deut. Chem. Ges. Ber., ix, 345).

This acid was extracted from the lichen *Zeora sordida* by chloroform or ether, the yield being about 9 per cent. Its composition was found to agree with the formula $C_{18}H_{16}O_7$: melting point 195°—197°. When heated to 150° with three or four times its weight of alcohol, it gives off carbon dioxide and is converted into *decarbusnic acid*, probably as represented by the equation—

$$C_{18}H_{16}O_7 + 2H_2O = CO_2 + C_2H_4O_2 + C_{15}H_{16}O_5.$$

Decarbusnic acid forms yellow silky needles, which turn reddish in the air, melt at 175°, and decompose at a higher temperature. It is soluble in hot alcohol, and sparingly in water and ether. It does not colour ferric chloride, but when heated to 200° with alcohol and water,

it yields an amorphous substance which colours ferric salts. Acetyl chloride does not act upon it. Nitric acid acts violently, forming oxalic acid. It reduces warm ammoniacal silver nitrate, with formation of an amorphous reddish-yellow substance.

When usnic acid is gradually heated to boiling with 2½ parts of 50 p. c. potash-solution in an atmosphere of hydrogen, and the brown solution is acidified with hydrochloric acid and then shaken with ether, this liquid leaves, on evaporation, *pyrusnic acid*, probably produced by the following decomposition :—

$$\underset{\text{Usnic acid.}}{C_{18}H_{16}O_7} + 3H_2O = CO_2 + C_2H_4O_2 + C_3H_6O + \underset{\text{Pyrusnic acid.}}{C_{12}H_{12}O_5}.$$

Pyrusnic acid forms brilliant scales melting at 195°, with partial decomposition, and is freely soluble in alcohol and boiling water. Its alkaline solutions rapidly absorb oxygen, turning green, and ultimately brown. The ammoniacal solution reduces silver nitrate very easily.

The ethereal extract of *Zeora sordida* contains, besides usnic acid, two neutral crystalline bodies, insoluble in water, amounting to about ·25 per cent. of the lichen:

*Zeorin*, $C_{13}H_{22}O$, sparingly soluble in alcohol, ether, and chloroform, melting at 230°—231°.

*Sordidin*, $C_{16}H_{18}O_7$, easily soluble in alcohol and ether, melting about 180°.

The lichen *Lecanora atra* gives up to ether, besides usnic acid, a substance which crystallises in yellowish scales, dissolves in alcohol and ether, and melts at about 91°. Its empirical formula is $C_{16}H_{18}O_5$.

J. R.

## Amido- and Diazophosphenylic Acids. By A. MICHAELIS and E. BENZINGER (Deut. Chem. Ges. Ber., ix, 513—517).

WHEN nitrophosphenylic acid is reduced by tin and hydrochloric acid, first a yellow bulky mass of stannous nitrophosphenylate separates out, which soon disappears again, and the solution likewise contains amidophosphenylic acid, a red body, which readily dissolves in alcohol.

*Amidophosphenylic acid*, $C_6H_4(NH_2)PO(OH)_2$, forms thin, white, glistening needles, which at 280° acquire a bluish-green colour, and undergo decomposition. 100 parts of water dissolve at 20°, and 0·52 pt. at 100° 0·4 pt. of the acid; in alcohol it dissolves but sparingly, and in ether not at all. When heated with soda-lime, it yields aniline and phosphoric acid. Sodium-amalgam acts on the nitro-acid like tin and hydrochloric acid.

The amido-acid dissolves readily in hydrochloric acid, and this solution is coloured red by bleaching-powder; on boiling, the colour remains.

The salts of the alkali-metals cannot be obtained pure, as they readily turn red. $C_6H_4(NH_2)PO(OAg)_2$ is a pale yellow precipitate, which is freely soluble in ammonia and nitric acid. $C_6H_4(NH_2)PO_3Cu$,

is a bluish-green powder dissolving in actic acid. $C_6H_4(NH_2)PO_3Pb$ forms a white amorphous precipitate.

When a hot solution of the amido-compound in nitric acid is for some time treated with nitrous acid and then concentrated, the nitrate of diazophosphenylic acid, $H_2PO_3.C_6H_4.N_2.NO_3$, separates out, which is purified by pressing and crystallisation from nitric acid. It forms white prisms, is freely soluble in water and alcohol, and sparingly in ether. It contains three molecules of water, of which two are given off at 130°; at 188° it melts, and at a few degrees higher explodes. The potassium-salt, $C_6H_4N_3O_3PO_3K_2 + H_2O$, is obtained as a precipitate consisting of small, yellow needles. The barium-salt, $C_6H_4N_3O_3PO_3Ba + 3H_2O$, crystallises from water in reddish-yellow glistening needles, which lose their water at 130°; it is very explosive. The silver-salt, $C_6H_4N_3O_3PO_3Ag_2$, is a red amorphous powder, which is very sparingly soluble. The aqueous solution of the free acid is very stable, and gives no nitrogen out on boiling; it does not show the reaction of nitric acid until it is boiled with an alkali.

C. S.

## Action of Soda-lime on Phosphenylic and Nitrophosphenylic Acids. By A. Michaelis and E. Benzinger (Deut. Chem. Ges. Ber., ix, 517—518).

When phosphenylic acid is heated with soda-lime, it is resolved into benzene and phosphoric acid. The nitro-acid, under the same conditions, yields aniline; most probably nitrobenzene was first formed, which, by the red-hot alkali, is reduced.

C. S.

## Action of Carbon Bisulphide on Ortho-amidophenol. By J. Dünner (Deut. Chem. Ges. Ber., ix, 465).

When an alcoholic solution of ortho-amidophenol is heated with excess of carbon bisulphide in a current of hydrogen, a yellowish crystalline body is deposited, whilst hydrogen sulphide escapes. The product dissolves in alcohol, ether, and acetic acid, and sparingly in water, and crystallises from alcohol in large nearly colourless needles which melt at 196°, and carbonise at a higher temperature. Its composition agrees with the formula $C_7H_5NSO$, and accordingly the reaction is represented thus:—

$$C_6H_4\begin{cases}OH\\NH_2\end{cases} + CS_2 = C_6H_4\begin{cases}OH\\N{=}C{=}S\end{cases} + H_2S.$$

The substance does not, however, possess the properties of a sulphocyanate. It dissolves in ammonia, but crystallises unchanged from the solution. Silver nitrate added to the ammoniacal solution throws down white flocks, which do not blacken on boiling. Boiling aniline decomposes the body, with evolution of hydrogen sulphide. Hydrochloric acid at 170° also decomposes it, carbon dioxide, hydrogen sulphide, and amidophenol hydrochloride being formed.

J. R.

**Action of Nitrous Acid on Acetanilide.** By OTTO FISCHER (Deut. Chem. Ges. Ber., ix, 463—465).

WHEN an excess of nitrous anhydride is passed into a cooled solution of acetanilide in glacial acetic acid, and the green solution is poured into water, a yellow body is precipitated, having the composition and properties of nitroso-acetanilide. The reaction, which is almost quantitative, is expressed by the equation—

$$\begin{matrix} C_6H_5 \\ C_2H_3O \end{matrix}\!\!>\!NH + HNO_2 = H_2O + \begin{matrix} C_6H_5 \\ C_2H_3O \end{matrix}\!\!>\!N—NO.$$

Nitroso-acetanilide is very unstable. When boiled with water, it first melts and then decomposes suddenly. It dissolves freely in alcohol, glacial acetic acid, and ether, but cannot be crystallised from the solutions. When heated on platinum foil, it explodes before melting. In a capillary tube it melts at 40°—41°, and decomposes completely at 46°. Reducing agents acting upon it regenerate acetanilide.

J. R.

**Methenyldiphenyldiamine.** By W. WEITH (Deut. Chem. Ges. Ber., ix, 454—458).

WHEN phenyl cyanide (phenylcarbylamide) containing aniline is boiled for an hour or two, a reaction takes place between the two bodies, the product being a body which distils above 250°, and solidifies on cooling. The composition of this product agrees with the formula $C_{13}H_{12}N_2$. It dissolves freely in hot alcohol and benzene, and crystallises therefrom in long needles, which melt at 135°—136°. It forms with hydrochloric acid a salt which crystallises in needles, and with platinum chloride an orange-yellow crystalline double-salt, having the formula $2(C_{13}H_{12}N_2.HCl).PtCl_4$. The body is identical with Hofmann's methenyldiphenyldiamine. Its formation and constitution are represented in the following equation:—

$$C_6H_5.N{=}C{=} + C_6H_5.NH_2 = C_6H_5.N{=}C\begin{matrix} \diagup H \\ \diagdown N \begin{matrix} \diagup H \\ \diagdown C_6H_5 \end{matrix} \end{matrix}.$$

Methenyldiphenyldiamine is formed also when a mixture of formic acid and aniline is heated for some time. The reaction may be expressed as follows:—

$$C\begin{matrix} \diagup H \\ {=}O \\ \diagdown OH \end{matrix} + 2(C_6H_5.NH_2) = 2H_2O + C\begin{matrix} \diagup H \\ {=}N.C_6H_5 \\ \diagdown N \begin{matrix} \diagup H \\ \diagdown C_6H_5 \end{matrix} \end{matrix}.$$

J. R.

## On β-Naphthylamine. By Fr. Palm (Deut. Chem. Ges. Ber., ix, 499—501).

The author has converted Liebermann and Scheiding's β-naphthylamine into *β-naphthol*, and thus obtained the direct proof, hitherto wanting, that it belongs to the group of β-naphthalene substitution-products. The conversion was effected by passing nitrous acid into a pulpy mass of β-naphthylamine and strong sulphuric acid, and boiling the resulting diazonaphthalene sulphate with water. The liquid deposited, on cooling, white laminæ of β-naphthol, which melted at 122°, and were not coloured by oxidising agents.

*β-Bromonaphthalene.*—Diazonaphthalene sulphate gives, on addition of bromine-water, a yellow crystalline precipitate of a perbromide, which, when boiled with alcohol, yields β-bromonaphthalene, $C_{10}H_7Br$. This substance crystallises in white shining laminæ, melting at 68°, is insoluble in water and potash, and is not coloured by oxidising agents.

*β-Chloronaphthalene* was obtained by boiling diazonaphthalene hydrochloride with strong hydrochloric acid. It forms white laminæ melting at 61°.

The following table exhibits the melting points of the known monosubstitution-products of naphthalene:—

| | α-series. | β-series. |
|---|---|---|
| $C_{10}H_7Cl$ | liquid | 61° |
| $C_{10}H_7Br$ | liquid | 69 |
| $C_{10}H_7Cy$ | 37° | 66 |
| $C_{10}H_7.OH$ | 94 | 122 |
| $C_{10}H_7.OC_2H_5$ | liquid | 33 |
| $C_{10}H_7.OC_2H_3O$ | liquid | 60 |
| $C_{10}H_7.SH$ | liquid | 137 |
| $C_{10}H_7.NH_2$ | 50° | 112 |
| $C_{10}H_7.NH.C_2H_3O$ | 159 | 132 |
| $C_{10}H_7.CO_2H$ | 161 | 181 |
| $C_{10}H_6.COCl$ | liquid | 43 |
| $C_{10}H_7.CONH_2$ | 204° | 192 |
| $C_{10}H_7.CO.C_6H_5$ | 75 | 82 |
| $C_{10}H_7.SO_2Cl$ | 66 | 76 |

J. R.

## A Vegetable Colouring Matter. By B. C. Mèderstadt (Dingl. polyt. J., ccxix, 165).

*Musa Fehii* belongs, like the bananas, to the family "Musaceæ," and grows on the island of Tahiti, especially on the hills. Several species are known. The fruit is good for food. The young trees yield a juice, coloured, syrupy, and adhesive, like gum. It is neutral to test-paper, and exhibits in thin layers a red, in thick layers, a blue violet colour. After being some time exposed to the air, it loses colour somewhat, and becomes mouldy. In well filled and closed bottles, it may be kept for months without any alteration, except the separation, after a long time,

of a violet glutinous substance, exactly resembling caoutchouc in its properties. The solution, separated from the caoutchouc, is miscible in all proportions with alcohol and water, and then shows a coloration so intense that a fivefold dilution with water produces no sensible alteration of tint. The taste is very astringent, and a gelatin-solution produces a considerable precipitate, carrying down the colouring matter with it, a proof that the latter exists in the solution in combination with tannic acid. Very weak alkaline solutions turn the solution green, without producing a precipitate. Calcium salts precipitate tannate, the precipitate carrying down the colouring matter with it. Weak acids produce a reddish tint. Iron salts, especially ferric sulphate, give a fine blue precipitate, ferrous acetate a black-blue precipitate like ink. Zinc and copper salts colour the solution blue, without giving any precipitate, but lead acetate gives a violet precipitate, and stannic chloride forms a bright violet lake. Organic bases (for example, cinchonine) precipitate the colouring matter from its solution. The filtrate evaporated to dryness, yields a *residual* blue powder, and the latter treated with alum solution, forms a dark blue lake, which keeps well in the dry state without alteration. The solution of this extract, freed from caoutchouc, gave with cotton mordanted with alum, a faint violet, inclined to grey, but when it was mordanted with tin-solution, a splendid violet was obtained. When iron was used as mordant, a full dark brown was produced. With silk, prepared with tin solution, a bright grey shade was the result.

W. S.

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## Researches on Buchu. By E. S. Wayne (Pharm. J. Trans. [3], 723).

In distilling the alcohol off from a partially exhausted lot of buchu, half of the last runnings dissolved in strong soda-solution, which, when treated with acid, yielded salicylic acid. When the buchu was distilled with water, salicylic acid was not detected, although the reaction was very similar; the author considers that the substance obtained by distillation with water yields salicylic acid when treated with alcohol; it is sparingly soluble in cold water, but soluble in alcohol and ether, giving a deep blue coloration with ferric chloride.

E. W. P.

## Chaulmogra Oil. By W. Dymock (Pharm. J. Trans. [3], vi, 761).

Standard samples of the oil were prepared, and compared with several commercial samples. The pure oil has a sp. gr. of 0·9; with a drop of strong sulphuric acid, the cold drawn oil forms a bulky, resinous mass round the drop, and after stirring, turns of a rich, olive-green colour, the resinous portion remaining separate and clear. If prepared by means of heat, the oil turns first of a burnt sienna colour, changing into olive green with acids. Other oils with which chaulmogra oil is likely to be adulterated, give a different shade of green with acids, thus :—

| | |
|---|---|
| Ground nut oil ..... | Turned light brown. |
| Cocoa-nut ..... | „ opaque white. |
| Castor oil ..... | „ dirty white. |
| Sesame ..... | „ pale dirty green. |
| Linseed ..... | „ dirty greenish-brown, bulky tenacious brown resinous mass also formed. |
| Several animal fats ..... | Turned different shades of brown. |

The oil of *Hydnocarpus Wightiana* has an odour resembling chaulmogra, but more acrid; the colour is greenish, not unlike some samples of cajuput oil. If kept long it throws down a white, fatty deposit, like that of chaulmogra. With sulphuric acid a tenacious resinous mass is formed in the cold drawn oil, and the rest turns of a light green colour. The boiled oil is of a deeper green colour, and with acid it first turns sienna brown, and afterwards a light green. The seeds of *Hydnocarpus* cannot be mistaken for those of *Gynocardia*; they are much smaller, flattened, and of a dirty white colour. The kernel is dark brown, like that of the *Gynocardia*.

E. W. P.

## Serum- and Egg-albumin and their Compounds.

By A. HEYNSIUS (Pflüger's Archiv. für Physiologie, xii, 549—596).

AFTER recapitulating the results of his former paper (this Journal [2], xiii, 469), the author brings forward objections to Schmidt's view, that albumin is a substance of itself soluble in water (see this Journal [2], xiv, 87—89). Schmidt obtained by dialysis a neutral liquid, which did not coagulate on heating, and contained no soluble ash-constituents. The author's objections to Schmidt's conclusion are:—

1. A neutral reaction does not necessarily mean entire absence of alkali, inasmuch as alkali can combine with egg-white without causing the reaction to become alkaline. This is proved by experiment. After long-continued dialysing a liquid was obtained, which became turbid at lower temperatures than that obtained after a shorter process of dialysing; because in the former case the alkali was more completely removed.

2. The failure of Schmidt to obtain any soluble salts from the liquid, which he regarded as a solution of pure albumin, is ascribed to the small quantity of material employed. It is shown by experiment that an amount of alkali, which is so small as to be unrecognised in the ash of such quantities of liquid as Schmidt employed, is sufficient to prevent coagulation of albumin (blood-serum and egg-white) on heating. A minute trace of acid also prevents coagulation.

$\frac{4}{10}$ths c.c. of $\frac{1}{1000}$ normal alkali (= 0·0000124 grm.) caused dialysed blood-serum to remain clear on boiling. 2 c.c. of the same solution (= 0·000062 grm. alkali) prevented coagulation of dialysed egg-white. $\frac{7}{10}$ths and $\frac{6}{10}$ths c.c. of $\frac{1}{100}$ normal acid solution respectively prevented coagulation in blood-serum and in egg-white.

It is further urged that the small quantity of alkali present in dialysed albumin will most probably be found in the insoluble ash, inas-

much as it is known that alkali—especially soda—when heated with phosphates of the earths, gives insoluble double salts.

The author concludes that, after the most careful dialysing, there is obtained:—1. A compound of albumin with calcium (and magnesium) phosphate, which is soluble in water, and from which albumin is precipitated on boiling. 2. That albumin free from salts cannot be obtained by dialysis, and that we are not therefore justified in saying that albumin is of itself soluble in water. 3. That with this compound there is associated (in the case of blood-serum, at least) a small quantity of albumin combined with soda, which alkali prevents to a greater or less extent, according to the quantity in which it is present, the coagulation alike of the albumin combined with itself, and of that combined with calcium phosphate, when the liquid is heated.

The compound of albumin with calcium (and magnesium) phosphate is possessed of the following properties:—

1. It is decomposed by acids and by alkalis, the albumin remaining in solution; the more concentrated the solution, the total quantity of albumin remaining unchanged, the greater is the quantity of alkali or of acid needed for decomposition.

2. It has an extremely faint acid reaction, becoming visible only after many hours.

3. Probably different compounds are formed, according as serum or egg-albumin is employed.

4. The compound is decomposed by warming; the longer dialysing has been continued, the lower is the temperature of decomposition; 50° was the lowest point noticed when distilled water was used in dialysing.

5. The decomposition temperature is raised not only by the addition of acid or alkali, but also by neutral salts.

There is no difference between the albumin obtained from this compound by the action of alkalis, and that found combined with alkalis in genuine egg-white.

The third part of this paper discusses the influence of alkalis and of acids upon albumins. It is shown that the quantity of acid or of alkali required to keep albumin in solution, on boiling, is influenced by the presence of neutral salts (NaCl was chiefly examined); that with a small quantity of sodium chloride the solvent influence of acids is marked, but with a large quantity of sodium chloride alkalis exercise a more distinctly solvent action. The albumin remains in these cases in the uncoagulated form. The stronger acids, as nitric, exercise a more marked solvent action than the weaker, as acetic, in the presence of an unvarying quantity of sodium chloride. Tables are given, containing the results of experiments with different acids and varying quantities of salts, especially sodium and calcium chlorides, upon albumin.

M. M. P. M.

## Bile-pigments. Part V. By R. MALY (Liebig's Annalen, clxxxi, 106—126).

THE author has obtained, by the action of bromine on bilirubin, a blue substance, which he calls *tribromo-bilirubin*. This body is best prepared by gradually adding a dilute solution of bromine in chloroform free from alcohol to bilirubin suspended in chloroform, when it is deposited as a nearly black mass. It is purified by dissolving it in alcohol and precipitating with water, and then forms a dark blue-green powder. Its composition, as determined by analysis, agrees with the formula, $C_{32}H_{33}Br_3N_4O_6$; and its formation is represented by the equation—

$$\underset{\text{Bilirubin.*}}{C_{32}H_{36}N_4O_6} + 3Br_2 = C_{32}H_{33}Br_3N_4O_6 + 3HBr.$$

Tribromobilirubin is insoluble in water. It dissolves easily in alcohol and ether, forming dark blue solutions, and sparingly in carbon bisulphide and benzene. Free acid added to the alcoholic solution turns it a brighter blue, as is also the solution in acetic acid. The substance dissolves in strong sulphuric acid, with dark green colour. It dissolves easily in alkalis, with violet colour. Strong potash, however, forms a green solution, which is due to partial decomposition of the substance, and consequent formation of biliverdin, $C_{32}H_{33}(HO)_3N_4O_6$. Tribromobilirubin is rapidly bleached by chlorine. Sodium amalgam added to its solution in alcohol and water, converts it into hydrobilirubin, $C_{32}H_{40}N_4O_7$.

J. R.

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## On the Possibility of the Disengagement of Free Nitrogen Gas during the Decay of Nitrogenous Organic Matter. By G. HÜFNER (J. pr. Chem. [2], xiii, 299—315).

ATTENTION has been previously directed to the presence of nitrogen gas among the products of the action of the pancreatic ferment upon fibrin. With the view of discovering, if possible, the source of this nitrogen, a number of experiments were undertaken to ascertain, in the first place, whether certain nitrogenous organic substances (fibrin, urea) could be gradually oxidised by gaseous oxygen at blood heat, with disengagement of nitrogen gas. The results of the experiments prove that the nitrogen in question does not originate in this way, but that its presence is due solely to leakage of air through the caoutchouc connection between the flask in which the decomposition takes place and the tube of the air-pump used for withdrawing the gases for examination.

H. H. B. S.

* The formula of bilirubin previously arrived at by Städeler and the author is $C_{16}H_{18}N_2O_3$, which the author now thinks should be doubled.

# Physiological Chemistry.

## Contributions to the Theory of the Decomposition of Albumin in the Animal Body. By J. FORSTER (Zeitschrift für Biologie, xi, 496—531).

THE author set himself to test the statement of Voit, that in the animal body the albumin composing the organs, Voit's organ-albumin, is of a relatively stable nature, whereas the nutrient solution of albumin circulating in the organs is constantly to a great extent undergoing decomposition.

With this view he introduced into the body of an animal a *living organ*, and estimated, both before and afterwards, the amount of the decomposition of albumin. In other words, he injected into the veins of a starving dog defibrinated blood, taken fresh from another dog. The blood forms the living organ, and the albumin composing the blood as a whole, is, according to the author, in the form of Voit's organ-albumin. He experimented further by introducing directly into the circulation solutions of albumin that had *not* traversed the digestive system.

His chief results are as follows:—

(1.) Blood introduced into the circulation of another animal of the same species is not decomposed at once, but persists in the same for a considerable time, and behaves in a manner similar to the blood already existing there. This is of some importance in regard to the practice of transfusion.

(2.) Solutions of albumin, which have not been subjected to the digestive process, when introduced directly into the circulation, are decomposed in the same manner and under like conditions, as the albuminous substances which are assimilated through the stomach and intestine.

(3.) The albumin contained in the body has not all the same tendency to decomposition, but two forms of it must be distinguished by (*a*) that which is firmly fixed in the organs and cells and is only slightly decomposed; and (*b*) the nutrient circulating albumin which is continually being in great part decomposed, and as constantly renewed by the nourishment.

E. C. B.

## Fermentation of the Liver, and Formation of Indol. By W. KOUKOL YASNOPOLSKY (Pflüger's Archiv. f. Physiologie, xii, 78—86).

THE observation of Liebig that the liver, when finely divided and suspended in water, ferments and gives off carbon dioxide and hydrogen gases, was extended by Béchamp, who showed that the same occurs when the liver has been washed in water containing phenol, and that the fermentation is independent of the presence of micrococci and bacteria.

The author shows that this process cannot be separated from that of putrefaction; but, nevertheless, that it exhibits certain striking peculiarities; and he confirms Béchamp's statement that the change does not depend upon the presence of the lower organisms. He also proves that indol is generated during the decomposition of albuminoïds in the organism, and that it is a normal constituent of urine.

T. S.

**Conjugated Sulphuric Acids in Urine.** By E. BAUMANN (Pflüger's Archiv. f. Physiologie, xii, 69—70).

A PRELIMINARY notice of the discovery that by the action of acids and warmth on urine, previously treated with barium salts to remove the sulphuric acid existing in the form of sulphates, a further production of sulphuric acid takes place in consequence of the decomposition of a conjugated sulphonic acid, and that the sulphate thus produced may exceed in amount the sulphate ready formed in the urine.

T. S.

**Recognition of Phenol-forming Substance in Urine.** By J. MUNK (Pflüger's Archiv. f. Physiologie, xii, 142—151).

THE author finds that herbivorous animals excrete in the urine a comparatively larger quantity of the substance, which, when this liquid is distilled with mineral acids furnishes phenol, and to which the term phenol-forming substance has been applied; also that in man and in carnivorous animals a vegetable diet increases the excretion of this phenol-forming substance.

Schultzen and Naunyn having stated that benzene when administered is excreted as phenol, this statement appeared to Munk to be extraordinary, seeing that benzene has never been directly oxidised into phenol outside the living body. He finds that when he himself takes benzene, neither this body nor phenol can be detected in his urine, but that the phenol-forming substance is thereby increased in proportion to the quantity of benzene ingested. The same was not found to be the case with toluene, this substance appearing in the urine as hippuric acid.

T. S.

**Composition and Possible Origin of the Gas from a Pyæmic Abscess.** By G. HÜFNER (J. pract. Chemie. [2], xiii, 326—330).

THE total volume of gas amounted to 5·56 c.m. The following are the results of the analysis:—

| | |
|---|---|
| Carbonic acid and traces of sulphuretted hydrogen | 1·05 per cent. |
| Oxygen | 14·50 ,, |
| Nitrogen | 84·45 ,, |

For the sake of comparison the author quotes the following results of three analyses of gases obtained from similar sources by Dressler:—

| | 1. | 2. | 3. |
|---|---|---|---|
| Carbonic acid | 14·0 | 14·49 | 10·31 |
| Oxygen | — | 0·83 | 2·15 |
| Nitrogen | 84·0 | 84·18 | 86·95 |
| Hydrogen | — | — | 0·09 (?) |
| Sulphuretted hydrogen | 2·0 | 0·50 | 0·50 |

Dressler assumed the nitrogen to be a product of the decomposition of nitrogenous organic matter. The author, on the contrary, believes all the gases to owe their origin to an accumulation of atmospheric air, followed by a process of oxidation.

H. H. B. S.

**Composition of the Air in the Soil and in Dwelling Houses.** By J. FORSTER (Zeitschr. f. Biologie, xi, 391—407).

A CONTRIBUTION towards the elucidation of Pettenkofer's well-known views respecting the generation of cholera and enteric fever. The author shows that a constant stream of air passes from the soil into our houses, and that we are thus placed in direct relation with the soil beneath us.

T. S.

## Analytical Chemistry.

**Simple Apparatus for the Analysis of Gases by Absorbent Solutions.** By F. M. RAOULT (Compt, rend., lxxxii, 844).

THE instrument consists of a graduated burette closed near each extremity with a tap; the upper end is continued, so as to form a sort of reservoir beyond the tap, the lower end terminates in a fine, almost capillary tube.

Between the lowest division and the bottom tap is a space of about 3 c.m. which is left filled with mercury, or water, after filling the tube with the gas to be examined. To use the instrument the reservoir is filled with an absorbent solution; the bottom tap is then opened to allow of the escape of a little of the fluid within the burette, thereby causing a slight minus pressure; the tap is then closed and the top one opened, whereby some of the absorbent solution is drawn in. After due agitation the top tap is opened again, and when the entrance of the water from the reservoir (with which the absorbent has been replaced) has ceased, the bottom tap is opened, whereby the liquid, as fast as it runs out of the burette, is replaced by fresh liquid running in at the top, which, flowing down the sides, thoroughly rinses the tube. No gas escapes during this washing. The pressure of the remaining gas is equalised with that of the atmosphere by laying the tube nearly horizontally, so as to bring the liquid within it into the upper portion of the tube against the top tap, which is then cautiously opened: a little

water gets forced out and the gas acquires the same pressure as the atmosphere. After allowing the tube to stand in a vertical position for a few minutes, the bulk of the gas is read off.

C. H. P.

## Titration of Normal Salts which have an Acid Reaction.

By C. WILLGERODT (Dingl. polyt. J., ccxx, 49—53).

IT is a well known fact that certain salts show an acid reaction, notwithstanding that all the hydrogen of their acid has been displaced by a metal. Such salts allow of being titrated by an alkali.

An aqueous solution having been prepared, some litmus is added, which immediately colours it red. A standard solution of alkali is then cautiously added from a burette, the final stage of the reaction being indicated by the usual change of colour to blue.

In this way some of the aluminium salts may be titrated, the precipitated $Al_2(OH)_6$ not seriously interfering with the colour if a sufficiently small quantity of the salt is taken for the determination. In the case of potassium alum, the decomposition may be thus represented :—

$$K_2Al_2(SO_4)_4 24H_2O + 6KHO = 4K_2SO_4 + Al_2(OH)_6 + 24H_2O.$$

The author has also applied this method of titration to the analysis of chrome alum and stannous chloride, and the results in each case are very accurate.

H. H. B. S.

## Use of Bromine on Hydrometallurgy, Assaying, and Chemical Technology.

By RUDOLF WAGNER (Dingl. polyt. J., ccxix, 544—546. *Conclusion.*)*

BERTHIER was probably the first to employ bromine in assaying; he made use of it for the assay of iron. A saturated aqueous solution dissolves the iron forming bromide, and converts the sulphur into sulphuric acid, and the phosphorus into phosphoric acid, the insoluble carbon or graphite being left behind as a residue.

Fresenius' method for the determination of sulphur in pig iron and steel (Zeitschrift für Analyt. Chem., 1878, 37) may be modified by passing the gases evolved during the solution of the iron in hydrochloric acid, through an aqueous or a hydrochloric acid solution of bromine, and thus converting the sulphur into sulphuric acid.

The use of bromine has been proposed for the determination of sulphurous acid in vitriol chamber gases, and the method is probably a practical one.

H. H. B. S.

* See previous abstract, *Journ. Chem. Soc.*, 1876, vol. i, page 741.

**Influence of the Asparagine contained in the Sugar Liquors from Beets and Canes on the Saccharimetric Determination; Destruction of the Rotatory Power of the Asparagine; Method of Determination.** By P. CHAMPION and H. PELLET (Compt. rend., lxxxii, 819).

THE rotatory power of ammoniacal solution of asparagine increases with the quantity of ammonia present. An aqueous solution of asparagine gave (by yellow light) a rotation of $-$ 6·14°, whilst one to which 10 per cent. by volume of ammonia was added gave a rotation of $-$ 10·41°. Mineral acids change the sign of rotation—a solution containing 10 per cent. by volume of aqueous hydrochloric acid, gave a rotation of $+$ 37·27°.

If some asparagine be added to a beetroot liquor, and the solution be treated with basic lead acetate, the filtered liquid, although alkaline, gives a greater $+$ rotation than the juice similarly treated, but without the asparagine, would afford.

The addition of acetic acid destroys the rotatory power of asparagine.

The over-estimation of the sugar in the juice may reach 0·7 per cent., due to the presence of the asparagine. The asparagine may be estimated by determining the rotatory power of the normal juice, and then again after the addition of acetic acid, and by a verification experiment, calculating the value of the difference of rotation by comparing the rotation of the normal juice, and then its rotation after the addition of a known quantity of asparagine. For example. Let the rotation of a given juice correspond with 300 divisions of the saccharimeter; after treatment with acetic acid, its rotation is reduced to 283; when treated with 2 per cent. of asparagine, its rotation is 325. Then, 325 $-$ 300 $=$ rotation due to 2 per cent. of asparagine; and 300 $-$ 283 $=$ rotation due to asparagine contained in the juice, from which 25 : 2 : : 17 : 1·36 the percentage of asparagine contained in the juice. The verification is necessary in every case, because the difference in the composition of the juices may modify the rotatory power.

C. H. P.

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**Note on the Examination of Whisky and other Spirits for Methylated Spirit and Fusel Oil.** By A. DUPRÉ (Pharm. J. Trans. [3], vi, 867).

FIVE ounces of the suspected spirit is distilled twice, in an apparatus having the receiver connected air-tight with a condenser, which is furnished with a mercury valve, to prevent evaporation, having been rendered alkaline the first time, acid the second time, and about two-thirds being distilled over each time. The distillate is then shaken up with dry potassium carbonate, and again twice distilled, half an ounce being driven over each time; this then contains any methyl alcohol that was originally present. This last distillate is diluted with water to a 10 per cent. strength, and the alcohol determined, 1st, by specific gravity; 2nd, by Geissler's vaporimeter; 3rd, by oxidation. The difference between the amount indicated by oxidation and that shown by specific gravity, gives a rough indication of the methyl alcohol present.

The vaporimeter gives higher results the greater the amount of methyl alcohol present. Should fusel oil be present, the spirit is oxidised by potassium dichromate, the excess of dichromate then reduced by zinc, and the acids distilled off; the acid distillate is then neutralised by a standard solution of soda, and then standard sulphuric acid, equal to one-twentieth of the soda employed, is added; the contents of the retort being then distilled at 130°, acid is again added, and the liquid distilled to dryness. The acid distillate, containing the acids higher in the series than acetic acid, is neutralised by barium carbonate, and evaporated to dryness. From the barium present the amylic alcohol may be calculated.

E. W. P.

## The Quantitative Estimation of Hæmoglobin in Blood.

By A. Rajewsky (Pflüger's Archiv. f. Physiologie, xii, 70—77).

A comparison was made of the various methods of determining hæmoglobin, devised by Hoppe-Seyler, Preyer, Brozeit, and Quincke.

Hoppe-Seyler's colorimetric is preferred to Preyer's spectroscopic method as being more exact. Brozeit's method of converting the hæmoglobin into hæmatin, and weighing the latter, is too tedious, Quincke's mode of using hollow prisms in the hæmatinometer was found to be rather more delicate than when blood is simply diluted in the hæmatinometer in the ordinary manner.

Though all the modes of determining hæmoglobin were found to be defective, the error with each method is almost constant, and may either be ignored or allowed for, so that very accurate estimations of hæmaglobin may be made.

In estimating hæmoglobin by the colorimetric method, a solution of picrocarmine may be substituted for the standard solution of hæmoglobin, and has the advantage of being constant.

T. S.

## On the Amount of Nitrogen and Albumin in Milk, and on the Estimation of Nitrogen in Albuminoïds.

By Leo Liebermann (Liebig's Annalen, clxxxi, 90—105).

The author has made a series of experiments, with the object of comparing the total amount of nitrogen in milk with the amount obtained in the form of albuminoïds by various methods of precipitation. His results are summed up as follows:—

1. By the methods of Brunner and Hoppe-Seyler, a considerable proportion of the albuminoïds escapes precipitation.
2. Haidlen's method gives the whole of the albumin.
3. Tannin completely precipitates the albuminoïds in milk.
4. Milk contains, besides casein and albumin, a third albuminoïd, differing from both.
5. Milk contains no nitrogenous substance other than albuminoïds.

In the above experiments the nitrogen was determined (1) by a modification of Will and Varrentrapp's process, the evolved ammonia being collected in a known quantity of hydrochloric acid, which was

titrated by a standard soda-solution; and (2) by the method of Dumas. In all cases the latter process gave about 34 per cent. more nitrogen than the former. Hence it is necessary, in estimating nitrogen in albuminous substances, to obtain it in the gaseous state.

J. R.

# Technical Chemistry.

## Sulphur in Coal Gas. By A. VÉRIGO (Compt. rend., lxxxii, 990—992).

COAL gas containing 2 grms. of sulphur in 100 English cubic feet was found to charge quickly with sulphurous acid the atmosphere of a room in which it was burnt. The sulphurous acid rapidly oxidised under these conditions into sulphuric acid, considerable quantities of which could be detected on objects in the apartment. The destructive action produced on goods and articles of furniture exposed to accumulations of sulphuric acid arising from this cause was proved in several ways.

R. R.

## Softening of Water. By W. KALMANN (Dingl. polyt. J., ccxix, 342).

THE method of Bérenger and Stingl, viz., treatment with calcium hydrate and caustic soda, is recommended. The following analyses of a water before and after the treatment, are given:—

| | CaO. | MgO. | $Na_2O$. | $Fe_2O_3$ and $Al_2O_3$. | $CO_2$. | $SO_3$. |
|---|---|---|---|---|---|---|
| Before.. | 1·265 | 0·832 | 0·030 | 0·006 | 1·360 | 0·883 |
| After .. | 0·038 | 0·134 | 1·244 | 0·005 | 0·029 | 0·911 |

| | Cl. | $SiO_2$. | Loss on heating. | |
|---|---|---|---|---|
| Before .. | 0·145 | 0·113 | 0·035 | = 4·669 |
| After .. | 0·183 | 0·060 | 0·033 | = 2·637 |

It was found that water which, after 14 days' use, caused the formation of a thick crust on boilers, might be employed for two or three months, after being subjected to the softening process, without bringing about the deposition of anything more than a slight slimy deposit, which could be easily removed.

M. M. P. M.

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## Removal of Gypsum from Water by means of Barium Oxalate. By F. ANTHON (Dingl. polyt. J., ccxix, 546).

THE quantity of barium oxalate necessary for the complete removal of gypsum from water does not depend merely upon the quantity of

gypsum present, but also to some extent upon the temperature and the length of time during which the barium salt is allowed to act upon the solution. The complete removal of 7·5 parts of gypsum by 17 parts of barium oxalate at 12°—15° temperature required 60 hours. At 37°—50° temperature, 3 hours; and at 94°—100° temperature, half an hour.

In all cases more than the theoretical quantity of barium oxalate must be used. For example, the removal of 7·5 parts of gypsum would require theoretically 10 parts of barium oxalate, whereas in practice it is found that even under the most favourable circumstances at least 16 parts are necessary.

H. H. B. S.

## Contamination of the Atmosphere by Trades and Factories.

(Dingl. polyt. J., ccxx, 87—89).

*Smoke.*—As a mean of 238 analyses, F. Knapp found in coal 1·7 per cent. of sulphur, of which no more than 0·2 per cent. remains in the ash. By burning 1,000 tons of coal, 15 tons of sulphur are sent into the air as sulphurous acid, which soon becomes converted into sulphuric acid. London air is said to contain 1·67 grms. of sulphuric acid in 1,000 cbm.; in Manchester 1,000 cbm. contain as much as 2·67 grms., the rainwater there contains about 0·001 per cent. of acid. Smith states that acidiferous air is injurious to the health of delicate constitutions, and he thinks that the bad effects it has on the mental activity have not been sufficiently considered. Plants suffer even more than men. According to Stöckhardt, pine-trees (Coniferæ) suffer more than leaved trees, such as birch, beech, oak, and fruit-trees. Schröder states that leaves absorb sulphurous acid from air containing only about 0·0002 vol. of acid; Smith, however, believes that the injuries to plants are caused merely by the damp air carrying down the acid, dry acidiferous air having no effect on plants. Steinhart mentions that for clamps and furnaces of old construction a distance of 70 to 125 meters, and for closed furnaces, with chimney 18 meters high, a distance of 35 to 50 meters will prevent the acid in smoke from damaging vegetation. Coke furnaces proved to be most injurious to plants; the effects were noticed at a distance of 250 meters. The smoke from brick kilns is less injurious, as the magnesia and lime of the clay retain the acid, clay containing pyrites will yield more acid.

*Flue-dust.*—According to Vivian, copper-smelting works evolve sulphurous acid, sulphuric acid, and compounds of arsenic and fluorine. In the preparation of lead about 12 per cent. or more of lead oxide is volatilised. Pelzner and Vohl have found in the bark and leaves of trees over 0·5 per cent. of oxides of the lead and zinc. Sulphurous acid and compounds of arsenic and zinc escape into the air and poison plants and animals fed therewith, in spite of the arrangements made for condensing these vapours. In 1864 the Halsberg and Mulden foundries near Freiberg had to pay about 55,000 marks of compensation, and after introducing in 1870 several improvements in their condensing apparatus they still had to pay 4,783 marks.

Leplay's calculations show that in South Wales alone, yearly, about

92,000 tons of sulphurous acid are sent into the air. A Belgian Select Committee state that from two sulphuric acid factories daily about 400 cbm. of sulphurous acid escaped into the air; and although with a well regulated method this loss will not be so great, still such contamination will never be entirely removed. By preparing 100 kilos. of ultramarine about 40 kilos. of sulphur are sent into the air, which Gentell proposes to use for the manufacture of sulphuric acid; but as the gas is not evolved regularly and is also very much diluted with other gases these difficulties will not be easily got over. According to von Dechen, in 1872, about 33,700,000 tons of coal were used in the German empire, which are equal to 1,000,000 tons of sulphurous acid.

*Sulphuretted hydrogen* is evolved by working up soda residues; the injurious effects of this gas have not been investigated sufficiently. It is also a constituent of putrid gases, which, arising from slaughter-houses, tanneries, glue and soap-works, are a nuisance to the neighbourhood. Putrid gases, however, are also evolved from closets, street-gutters, and from the soil of large cities in such quantities that the gases escaping from well managed chemical works are comparatively insignificant.

D. B.

## A Peculiar kind of Steam Boiler Corrosion.

By V. Wartha (Dingl. polyt. J., ccxix, 212—254).

It was observed in a works in Hungary that a short time after commencing work, everything being new, the "heater" associated with the steam boiler began to leak, and so much so that it was necessary to change it. It was found that the wrought boiler plate of this apparatus (7 mm. thickness) was quite perforated in some parts, in others corroded to a depth of 4 mm. The inner and actual boiler plate was quite intact, and covered with a scarcely perceptible layer of calcium carbonate, &c.

On examination it was found that the corroded parts were filled up with a brown fatty substance, which was found to contain mostly ferric oxide, together with considerable quantities of a fatty substance, some carbon, and mineral matter. The fatty substance was treated with ether, which extracted a dark brown fatty body, remaining behind on evaporating the ether as a brown greasy mass, insoluble in water, and undoubtedly ferric oleate. No glycerin could be detected. On making a synthetical experiment with free oleic acid, the following results appeared:—A few cubic centimeters of this fatty acid were brought together with water and some iron filings, when, on heating, hydrogen gas was energetically evolved, whilst a brown greasy ferric compound was formed, soluble in ether. This body contained 11 per cent. of ferric oxide, and appeared exactly similar to the residue from the "heater." The explanation of the mystery now became simple. In the works mentioned, the "spent steam" was returned to the "heater" for economy sake, and thus free oleic acid, from oily matter decomposed by the heat and pressure of the steam cylinder, also accompanied it. The drops of condensed oleic acid adhering to the iron plate would soon commence action, and become saturated with

ferric oxide. This iron compound now suffers decomposition in contact with the hot water under pressure, and is split up again to ferric oxide and free fat acid. A circular action is thus set up of an insidious kind, whereby a relatively small quantity of oleic acid can actually bore its way through a 7 mm. boiler plate.

W. S.

## On Potash.

By H. GRÜNEBERG (Dingl. polyt. J., ccxix, 254).

IT is remarkable that the three great sources of potash which have been discovered within the last twenty years are the animal, vegetable, and mineral kingdoms:

1. The carbonised residue of beetroot molasses.
2. The residues from the washing of sheep's wool.
3. The Stassfurt deposit of potassium salts.

The manufacture of potash salts from beetroot residues is the oldest operation of the three indicated above, that from sheep's sweat is of recent date. The manufacture of potash by Leblanc's process from the sulphate is also of recent date. The drawback in the latter method is the volatility of the potassium salts. This tells considerably in the "black-ash" process, and these losses can be ill-sustained, on account of the value of the article. This volatility at a high temperature exceeds that of the sodium salts. The author has devised a method by which the potassium chloride of the Stassfurt deposit, by double decomposition with magnesium sulphate (also occurring in this deposit), is converted into potassium sulphate. The reaction takes place in several stages:

1. By the action of a hot magnesium sulphate solution upon potassium chloride:

$$3KCl + 2MgSO_4 = MgSO_4.K_2SO_4 + KCl.MgCl_2.$$

2. By treatment of the hot solution of the above double salt with potassium chloride, or by macerating the undissolved double salt with a cold potassium chloride solution:

$$K_2SO_4.MgSO_4 + 3KCl = 2K_2SO_4 + KCl.MgCl_2.$$

3. Decomposition of the double salt, $KCl.MgCl_2$, by maceration with cold water.

The magnesium chloride acted very injuriously, in hindering by its presence the rapid and exact decomposition of the salts in their reaction upon one another. The potassium sulphate thus obtained was a fine crystalline powder, and of great purity. For the conversion into sulphate by means of sulphuric acid, the author considers it most advantageous to use the beetroot residues containing potassium chloride with from 10 to 12 per cent. of potassium sulphate already, and tolerably free from sodium salts. He also recommends the use of the potassium sulphate obtained from "kelp." The fusion of the potassium sulphate with limestone and coal ("black-ash process") is carried out just as in the case of soda, but it is especially necessary here to avoid too high

a temperature. With coals very rich in nitrogen, potassium ferrocyanide is formed in the black-ash process in such quantity that it pays to extract it. The salt separates on evaporation of the carbonated lies at 50° Baumé, together with undecomposed potassium sulphate. A double recrystallisation makes the salt quite marketable.

The "potash" (potassium carbonate) prepared from the sulphate is very pure, containing on the average 92 to 93 per cent. of potassium carbonate, and as impurities 2 to 3 per cent. soda, 2 per cent. potassium chloride, and 1 to 2 per cent. potassium sulphate. It is thus superior to the Russian potashes, which only contain 68 to 70 per cent. of potassium carbonate.

The following list exhibits the different kind of potashes of best quality which come into the market:—

| Origin. | Quality. | Potassium carbonate with hydrate calc. to carbonate. | Sodium carbonate. | Potassium sulphate. | Potassium chloride. |
|---|---|---|---|---|---|
| America ..... | 1 | 104·4 | 1·4 | 4·0 | 2·0 |
| " ..... | 2 | 71·2 | 8·2 | 16·1 | 3·6 |
| American pearlash.... | — | 71·3 | 2·3 | 14·3 | 3·6 |
| Tuscan potash ..... | — | 74·1 | 3·0 | 13·4 | 0·9 |
| Illyrian " ..... | — | 89·3 | 0·0 | 1·2 | 9·5 |
| Russian " ..... | — | 69·6 | 3·0 | 14·1 | 2·0 |
| Siebenbürger potash .. | — | 81·2 | 6·8 | 6·4 | 0·6 |
| Hungarian house ashes | — | 44·6 | 18·1 | 30·0 | 7·3 |
| Galician potash ..... | — | 46·9 | 3 6 | 29·9 | 11·1 |
| Refined sheep-wash ashes ..... | — | 72·5 | 4·1 | 5·9 | 6·3 |
| French beetroot ash .. | 1 | 90·3 | 2·5 | 2·8 | 3·4 |
| " " " .. | 2 | 80·1 | 12·6 | 2·5 | 3·4 |
| German potash ..... | 1 | 92·2 | 2·4 | 1·4 | 2·9 |
| " " ..... | 2 | 84·9 | 8·2 | 2·8 | 3·5 |

Numbers are given showing that the Russian export of potash has diminished to one-half of what it was ten years ago, the American to one-fifth, their decline being considered undoubtedly due to the discovery and working of the stores already mentioned.

W. S.

## Lucifer Match Compositions.

By H. Schwarz (Dingl. polyt. J., ccxix, 243—245).

Two kinds of lucifer matches were experimented upon. The first was of Vienna manufacture, and consisted of splinters of wood impregnated with rosin, and having brown heads, which ignited exceedingly well. Analysis gave lead peroxide, lead nitrate, red lead, phosphorus, and sulphur, with dextrin-gum to bind the ingredients together.

The heads were cut off and boiled with nitric acid. The greater part of the mass dissolved. The liquid was filtered to separate woody fibre, the filtrate made up to a convenient known volume, one part

taken for the lead estimation, the other for the phosphorus (by means of molybdic acid). The sulphur was estimated by dissolving another portion of a match in a little nitric acid, mixing with water without filtration, and precipitating the lead with hydrogen sulphide, after which the sulphuric acid was determined by barium chloride in the filtrate, taking the precaution first to drive off nitric acid by evaporation. No permanent residue remaining on ignition, neither nitre nor potassium chlorate could be present in the mixture.

Very good matches, quite corresponding with the above, were furnished by the following proportions:—1 part of flowers of sulphur was melted under warm water with 4 parts of yellow phosphorus. Most of the water was poured off, and the fluid phosphorus sulphide was intimately triturated with 4 parts of dextrin-gum. Then 45 parts of red lead were decomposed with 1½ equivalents of nitric acid, the mixture evaporated to dryness, pulverised, and added little by little to the phosphorus mixture, and mixed with it. The match-stems were saturated with an alcoholic pine-resin solution (these stems previously being slightly charred), and were finally dried at a moderate temperature. They ignite excellently.

The second kind have four-sided stems, saturated with paraffin. They appear to be of Swedish manufacture, and ignite on every surface. They have also bright blue heads, igniting with a considerable detonation on friction. Analysis proved the presence of potassium chlorate, yellow phosphorus, calcium carbonate and sulphate, glass-powder, and gum. The gypsum was formed accidentally by the action of the sulphuric acid in the indigo-sulphate, acting upon the calcium carbonate used to diminish the detonation of the potassium chlorate. The following are the composition and the probable proportions used for this match composition:—

| | Per cent. | Probable proportions. | |
|---|---|---|---|
| Phosphorus..... | 3·15 | Phosphorus ..... .. | 1 part |
| Calcium carbonate.... | 15·78 | Chalk ..... | 5 parts |
| „ sulphate .... | 8·90 | Gypsum ..... | 2·8 „ |
| Glass-powder ..... | 18·62 | Glass-powder ..... | 6 „ |
| Potassium chlorate .. | 35·40 | Potassium chlorate.. | 11·2 „ |
| Organic matter and loss ..... | 18·15 | Agglutinating and colouring matters | 6 „ |
| | 100·00 | | |

The phosphorus was melted under the gum-solution, and then the chalk, glass-powder, and indigo-sulphate added, the latter in considerable excess to compensate for the bleaching action of the phosphorus. These were all rubbed together, carbonic acid being liberated; and lastly, the finely powdered potassium chlorate was gradually mixed in. This composition inflames with an explosion on sulphurised matches, but answers best on matches impregnated with paraffin. It acts with great certainty and is not liable to injury by damp.

W. S.

**The Manufacture of Ultramarine.** C. FÜRSTENAU (Dingl. polyt. J., ccxix, 269—272).

ACCORDING to the author's view, ultramarine is an alumino-sodium silicate, in which a part of the oxygen is replaced by *sulphur*. Many observations have proved that only two aluminium silicates are suited for the preparation of ultramarine, viz., $2Al_2O_3.3SiO_2$ and $Al_2O_3.2SiO_2$. These give, on treatment with di- or pentasulphide of sodium, colours of the following properties :—

(*a.*) $2Al_2O_3.3SiO_2$ with $Na_2S_2$—pure clear blue, but with little depth of tint.

(*b.*) $2Al_2O_3.3SiO_2$ with $Na_2S_5$—pure dark blue and very deep-tinted.

*a and b do not contain alum.*

(*c.*) $Al_2O_3.2SiO_2$ with $Na_2S_2$—light reddish colour, a little dirty.

(*d.*) $Al_2O_3.2SiO_2$ with $Na_2S_5$—dark violet-blue, very beautiful and deep in tint.

*c and d do contain alum.*

Kaolins, which contain alumina and silica in other proportions, yield mixtures of different ultramarines, and, if corresponding to *c* above, muddy colours are produced. In the choice of kaolin, special care must be taken to avoid untempered clays, or those containing finely-divided stony matter; with such kaolin, no pure colours are obtainable. For regulating the amount of silica, either finely-ground and washed quartz, or washed and ignited siliceous-earth ("kieselguhr") is used.

The following proportions were found useful :—

(*a.*) For a pure blue article :—

$$2Al_2O_3.3SiO_2 + 4Na_2CO_3 + 4C + 7S.$$

(*b.*) For reddish, aluminous, deep-tinted varieties :—

$$Al_2O_3.2SiO_2 + 4Na_2CO_2 + 8C + 16S.$$

In formula (*a*), the soda may be replaced by Glauber's salt, with addition of enough carbon to take up all the oxygen of the salt, and to form carbon monoxide. These colours are bright, and have very little depth. After a considerable amount of experience and observation, the author has come to the conclusion, that it is impossible in one roasting, either in pots or in the reverberatory furnace, to obtain a product needing no further operation to develop the full blue colour. On this account, reverberatory furnaces are now used, divided into three parts, one for drying, one for burning blue, and the other for roasting. The usual capacity of such a furnace is 30 to 35 cwt. Raking-out time, 36 hours. Time of cooling, 10 days.

The Glauber's salt ultramarine must, at this stage, be well sorted, and all white pieces placed again in the original mixture, the remainder is roasted, and then treated as usual.

After another process, the green, unwashed substance is ground wet, then boiled with water, washing some eight times. It is then dried, sieved, and lastly roasted, and then packed. The working through the

furnacing-stage occupies 35 days. A reverberatory furnace furnishes about 15 cwt. of blue in 14 days. The main reason of the preference for this furnace is the limited size of the pot-furnace, and the unequal product it gave, so that three or four varieties were found as the result of each roasting. The author was, therefore, led to construct a pot-furnace which would accommodate 32 to 40 cwt. of mixture. The furnace is raked out in 8 hours at the longest, and requires two days for the cooling, so that a raking-out can take place twice a week. Such a furnace yields, in 14 days, 75 cwt. of blue against 15 cwt. in the same time by a reverberatory of similar dimensions. In the round-furnace, the green obtained is roasted with sulphur as usual. By using steam, this operation has become quite safe.

W. S.

## On the Development of the Ultramarine Manufacture.

(Dingl. polyt. J., ccxx, 53—60).

SINCE the year 1862, the number of ultramarine manufactories has increased by seven in Germany and by one in Austria, but has remained the same in Belgium and France. The production has increased in the proportion of 100 to 240, but this is principally due to those German factories that were in existence in 1862. The following table shows the development of this industry between the years 1862 and 1872:—

| | 1862. | | 1872. | |
|---|---|---|---|---|
| | Number of factories. | Production. | Number of factories. | Production. |
| | | *t.* | | *t.* |
| Germany | 16 | 2754 | 23 | 6579 |
| France | 6 | 527 | 6 | 1156 |
| Belgium | 1 | 175 | 1 | 450 |
| Austria | 1 | 100 | 2 | 400 |

There is, besides, one factory in England and one in North America.

H. H. B. S.

## Kainite from Kalusz (Galicia). By H. SCHWARZ

(Dingl. polyt. J., ccxix, 345—360).

THE analysis of two samples of the mineral gave the following results:—

| | $K_2SO_4$. | $MgSO_4$. | NaCl. | $MgCl_2$. | $Al_2O_3$. | $H_2O$ and loss. |
|---|---|---|---|---|---|---|
| A. | 22·12 | 18·21 | 29·02 | 12·79 | 2·38 | 16·05 |
| B. | 22·77 | 17·20 | 23·92 | 14·60 | 5·65 | 15·86 |

It was attempted to remove the magnesium and sodium chlorides by washing with cold water, and then to dissolve the remaining schönit

($K_2Mg(SO_4)_2.6H_2O$) by solution in hot water: this method was not, however, successful. Other methods for obtaining pure potassium sulphate were, also, without success, but eventually it was found that treatment of an aqueous solution of the mineral with gypsum caused the formation of a double sulphate of potassium and calcium, which could be readily collected and pressed, so that the whole, or almost the whole, of the magnesium and sodium chlorides were removed. On boiling this double-salt with water, potassium sulphate goes into solution, while gypsum remains, and may be again employed.

M. M. P. M.

**Manufacture of Alum under Pressure.** By M. FAUDEL (Dingl. polyt. J., ccxix, 365—366).

THE author recommends, for the use of the paper-maker, alum-cake prepared by heating China clay with sulphuric acid under a pressure of 2 to 2½ atmospheres in leaden vessels. 1·5 parts of clay, heated to 135°—140° under a pressure of 3 to 3½ atmospheres, with 1·8 parts of sulphuric acid of 1·525 sp. gr., yielded a cake which dissolved almost entirely in water, and had the following composition:—

| Water and impurities. | Aluminum sulphate. | Silicic acid. | Free sulphuric acid. |
|---|---|---|---|
| 37·5 | 37·0 | 19·5 | 6·0 = 100·0. |

The free acid may be neutralised by addition of alumina.

M. M. P. M.

**Decarbonisation of Spiegeleisen by Heat.** By R. W. RAYMOND (Dingl. polyt. J., ccxx, 60—64).

THE use of ordinary spiegeleisen in the Bessemer process has a double object, firstly, the re-carbonisation to the requisite degree of the partially or almost completely decarbonised raw iron; and secondly, the prevention of the formation of "red-short" iron. The author ascribes this latter deleterious property to the presence of oxide of iron in the molten metal, and he assumes, further, that the manganese contained in the spiegeleisen combines with the oxygen of the oxide of iron, and in this way passes into the slag. A trifling quantity of manganese is, however, retained by the cast steel, and probably co-operates to the improvement of its quality. Whatever explanation is accepted, it is certain that the action of manganese is not merely favourable, but absolutely necessary. But, by the use of spiegeleisen very rich in carbon, the quantity of manganese is limited, since for the production of soft steel, only a moderate amount of carbon can be introduced. The necessity, therefore, of the addition of manganese without a simultaneous introduction of an excess of carbon, has led to the substitution of ferromanganese for spiegeleisen, and the only objection to its use lies in the high price of this alloy. A short time ago, the author's attention was directed by Prof. Brown to the possibility of adapting the process of long heating employed in manufacturing malleable iron to the decarbonisation of spiegeleisen, so as to produce

a raw iron rich in manganese but containing only a small proportion of carbon. The following analyses made by J. B. Britton, show the change in composition produced in spiegeleisen by such treatment:—

| | Unignited. | Ignited. |
|---|---|---|
| Phosphorus | 0·079 | 0·055 |
| Manganese | 11·636 | 10·698 |
| Carbon | 3·016 | 0·499 |

(See also *J. Chem. Soc.*, 1876, vol. i, page 453).

H. H. B. S.

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## Analysis of White Fumes from a Blast-furnace near Longwy.

By L. Gruner (Compt. rend., lxxxii, 559—562).

The ores used in the furnace are ferruginous oolite, with a matrix of clay-slate. They are reduced with coke, and with a blast heated to 500°—600°, in order to obtain black or grey pig-iron, like that from Scotch furnaces. Owing to the high temperature of the blast, a dense white smoke is evolved which incrusts the walls of the work. The portion soluble in water consists largely of potassium sulphate, but no sulphide; but the insoluble part evolves sulphuretted hydrogen on treatment with an acid. On analysis, the deposit was found to have the following composition:—

| | | | |
|---|---|---|---|
| Portion soluble in water. | $K_2SO_4$ | 37·82 | = 43·36 |
| | $K_2CO_3$ | 3·90 | |
| | KCl | 1·52 | |
| | Soluble $SiO_2$ | 0·12 | |
| Portion insoluble in water. | $SiO_2$ | 22·98 | = 53·00 |
| | CaO | 15·88 | |
| | $Al_2O_3$ | 9·62 | |
| | FeO | 4·00 | |
| | MnO | 0·16 | |
| | MgO | 0·36 | |
| | S | not estimated | |
| Hygrometric water | | 3·20 | = 3·20 |
| | | | 99·56 |

The analysis of the insoluble portion, not including sulphur, is compared with that of the furnace slag—

| | Insoluble portion. | | Slag. |
|---|---|---|---|
| $SiO_2$ | 43·3 | | 33·0 |
| CaO | 30·0 | | 43·7 |
| $Al_2O_3$ | 18·1 | | 14·6 |
| FeO | 7·6 | | 3·6 |
| MuO | 0·3 | | |
| MgO | 0·7 | | 1·9 |
| | | $K_2O$ | 1·7 |
| | 100·0 | S | 0·7 |
| | | $H_2SO_4$ | 0·2 |
| | | | 99·4 |

As the slag is more basic than the insoluble portion, it would appear that the latter is mixed with free silica; and on examination, it was found to contain fibrous silica, which may have been evolved as silicon sulphide, which, on exposure to moist air, is decomposed into fibrous silica. The potassium sulphate is probably owing to the oxidation of volatilised potassium sulphide.

W. R.

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## The Application of Phosphorus to the "Poling" of Copper.

By W. WESTON (Phil. Mag. [5], i, 542—543).

THE effect of the addition of phosphorus to copper is to "pole" it, and to increase its density. In practice, the metal is brought near to the tough-pitch point by the phosphorus (which is added in the form of a phosphide of copper containing about 7 per cent. of phosphorus), and the poling finished in the usual way. The quantity of phosphorus added corresponds to about ·07 per cent., of which about one-half is retained. The advantages gained by the use of the phosphorus are—1. Increased density of copper. 2. Acceleration of poling process. 3. Diminished consumption of poles.

C. H. P.

## Notes on Hydrometallic Copper Extraction.

By G. LUNGÉ (Dingl. polyt. J., ccxix, 323—330).

THE sodium sulphate produced in the process of extracting copper by washing with common salt, may be obtained in a state of almost perfect purity by evaporating the acid mother-liquor from the precipitated copper to dryness, grinding to fine powder, and heating until the iron salts are completely oxidised. On then dissolving the mass in water by the aid of heat, the ferric oxide remains undissolved and may be collected in a state fit for sending into the market. The liquid is boiled down by steam, with constant agitation, and the sodium sulphate crystallised out. The process pays only where fuel is cheap and sodium sulphate and ferric oxide valuable.

In a second part of this paper, the process of preparing spongy iron is minutely described: there appears to be nothing new.

M. M. P. M.

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## Method for Finishing Bronze and Brass Articles.

By F. DIETLEN (Dingl. polyt. J., ccxx, 90).

IF the articles are ready-mounted and not soldered, they are slightly heated to remove all fat. If they cannot be heated, they are washed with a solution of potash or soda, dried with sawdust, etched and polished, using water but not fat. They are now cleaned with chalk, warmed, and varnished. Equal parts of sulphuric and nitric acids, with some zinc, form the etching solution. If the articles are made of light or greenish brass, they must be dyed red by boiling them in a solution of tartar. The varnish is prepared by dissolving 65 grams of shellac in a mixture of 0·5 litre of alcohol, adding 4 tablespoonfuls of

turmeric-meal. After allowing the mixture to stand at a warm place for 24 hours, it is filtered through felt and ready for use.

D. B.

## Recovery of Aldehyde in the Manufacture of Sugar of Lead.

By E. DOLLFUS (Dingl. polyt. J., ccxix, 92).

IN the process for preparing acetic acid by the oxidation of spirit of wine by means of atmospheric air, some aldehyde is always formed. By careful working, the quantity of this product can be kept at an insignificant figure, but this is always great enough. With good arrangements, if the acid be converted into sugar of lead, all this aldehyde ought to be recovered. In the manufacture of sugar of lead, hot acetic acid vapours are passed through copper vessels with perforated false bottoms, on which litharge is placed. Aqueous vapours are liberated, and escape during the process; and amongst the first portions, the odour of aldehyde is perceptible. By condensing these aqueous vapours, the author succeeded in obtaining a certain quantity of aldehyde in dilute aqueous solution. He points out how easily arrangements might be made for condensing these aqueous vapours containing aldehyde, and then strengthening and purifying the product.

W. S.

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## Egg-albumin and Blood-albumin.

By G. WITZ (Dingl. polyt. J., ccxix, 84).

BLOOD and the eggs of poultry are the chief sources of the albumin used by the calico-printer. An inquiry is made with respect to these sources, and to the amounts of pure albumin contained in them. The gross weight of a hen's egg varies from 45 to 60 grams, but there are occasionally large ones which weigh 69 grams, consisting of shell, 8 grams; white, 41 grams; yolk, 20 grams. The proportion between white and yolk is also variable, the amount of white increasing in the spring, the amount of yolk in the summer. The author obtained the following results as to the amount of albumin furnished by eggs. Without making any difference between large or small kinds, 366 eggs yield a mixture, which on standing deposits 10 per cent. of impurities, and furnishes 1 kilo. of pure dry albumin. This number of eggs yields also about 4 kilos. of yolk. Yolk of egg has of late been more and more used in the leather industry.

In the year 1860 the annual consumption of albumin in the Alsacian printing industry alone (with about 100 machines) amounted to 125,000 kilos., representing 37,500,000 eggs,—the produce of 250,000 hens. The Alsacian manufacturers, therefore, offered a considerable sum for the discovery of a good and cheap substitute for egg-albumin. This problem is not yet solved. Casein and gum yield colours of little solidity, also the proposal of Leuchs to replace the egg-albumin by fish-spawn has been found of no avail, on account of the impurities contained in the latter substitute. Blood-albumin has, however, made considerable way in the estimation of the manufacturers as a substitute for the egg-albumin, but it cannot be used as a complete substitute, as

it is too strongly coloured for the production of very fine shades. It has been calculated that *the blood* of one ox or cow furnishes 4 litres of serum, or 400 grams of dry albumin. The serum of a calf's blood furnishes 82 grams of dry albumin per litre. The albumin from sheep's blood thickens better than that from the blood of oxen, with an equal yield of serum, but it is more strongly coloured. 1 kilo. of albumin represents 2½ oxen, 10 sheep, or 17 calves. More recent results show that from one ox it is possible to prepare 750 to 800 grams of blood albumin; from a calf, 350 to 400 grams; and from a sheep, 200 grams. The author calculates that Paris with its 1,851,792 inhabitants might furnish, according to the present consumption of meat, 300,000 kilos. of blood-albumin per annum, at 4 marks per kilo., and thus there would be given back 72,000,000 eggs. It may be considered that the annual meat consumption of six inhabitants of a great city makes possible the production of 1 kilo. of blood-albumin.

W. S.

**Solid Albumin (with 15 p. c. Hygroscopic Water) in White of Egg-solutions at 17·5°.** By G. WITZ (Dingl. polyt. J., ccxix, 93).

| Albumin in 100 parts. | Baumé. | Sp. gravity. |
|---|---|---|
| 1 | 0·37 | 1·0026 |
| 2 | 0·77 | 1·0054 |
| 3 | 1·12 | 1·0078 |
| 5 | 1·85 | 1·0130 |
| 10 | 3·66 | 1·0261 |
| 15 | 5·32 | 1·0384 |
| 20 | 7·06 | 1·0515 |
| 25 | 8·72 | 1·0644 |
| 30 | 10·42 | 1·0780 |
| 35 | 12·12 | 1·0919 |
| 40 | 13·78 | 1·1058 |
| 45 | 15·48 | 1·1204 |
| 50 | 17·16 | 1·1352 |
| 55 | 18·90 | 1·1511 |

W. S.

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**Regeneration of Spent Albumin by means of Pepsin.** By J. WAGNER and G. WITZ (Dingl. polyt. J., ccxix, 166—171).

THE property of an aqueous solution of albumin, to deposit the albumin in the insoluble form on application of heat, is applied to the fixing of a variety of important colours upon cotton. Both soluble and insoluble colours are mixed with the cold solution, printed on the cotton-piece, and the latter is then steamed, which converts the soluble albumin into the insoluble variety, forming a kind of fixed and elastic varnish upon the cloth, and mechanically fixing the colouring matter. Both egg- and blood-albumin pass into the insoluble form, *either wholly or partially*, if the temperature of the drying chamber has passed 35°, or even if exposed to the sun accidentally, or after allowing it to stand too

long. Now the problem has been, "How to recover albumin which has thus become insoluble and is lost, so as to obtain it again in the soluble form for further service." Dilute alkaline carbonates or hydrates could bring such albumin into solution again, but such a solution lacks the power of coagulating on application of heat; in fact the constitution of the albumin is altered by the alkalis, a portion of its sulphur being abstracted, and the substance in solution is therefore not albumin at all. This prejudicial action of alkalis is at times experienced in working; thus if the basic lead chromate be not completely freed by washing, from adhering lime, and be then thickened with albumin and printed, not a bright orange is obtained on the cotton on steaming, but, through presence of lead sulphide, a muddy-brown. At length J. Wagner devised the following successful method:—He brought 350 to 400 grams of such unserviceable albumin in contact with 30 grams of calf's stomach, cut into little pieces and distributed through 1 litre of water. The water was treated with 10 grams of concentrated hydrochloric acid, and had a temperature of 37·5°. After 24 to 36 hours' standing the whole was passed through a fine sieve, and the filtrate neutralised with ammonia, and thus an albumin solution was obtained which answered every purpose completely. Witz uses a sheep's stomach, and to 1 litre of acidified water nearly 125 grams of dry insoluble albumin. He states that pigs' stomachs are even more active than sheep's. He further digests for 40 hours at a temperature of 35° to 40°, whereby somewhat more than half the albumin goes into solution. The dissolved portion being separated by a sieve, the insoluble portion is treated once more with acidified water in the same manner, to bring a further portion of albumin into solution. The solution so obtained is without odour, and but little coloured, a fact worthy of note as regards blood-albumin. It has also the property, after neutralisation by ammonia, to become coagulated either by boiling or by addition of alcohol. Experiments as to the use of this albumin in ultramarine printing, showed that on steaming, a pure, fast blue is obtainable, unaffected by boiling soap solution. There is one reaction which marks a difference between albumin recovered by pepsin and ordinary albumin. The former treated with acetic acid, before or after neutralisation with ammonia, either does not at all become turbid, or only slightly, and in no case gelatinises, even after long standing. On the contrary, one part of egg-albumin dissolved in ten parts of water, so that the filtered solution has a sp. gr. of 1·027, and treated with an equal or half volume of acetic acid of sp. gr. 1·050, immediately forms a solid, transparent jelly. This also takes place if hydrochloric acid be added. Witz has proved conclusively that under no circumstances whatever is coagulated albumin soluble in acetic acid. The text-books usually state that albumin-solutions are not precipitated at all by acetic acid, and are thus in great error. Digestion with pepsin is thus a certain method of bringing coagulated albumin again into solution. Just as cloth, which has undergone some injury in finishing, may be quite freed from its size by digestion with malt, and much more easily than by long treatment with boiling water, so by the help of pepsin, printed albumin colours, even after steaming, can be completely removed from the fabric.

For this purpose the piece is placed in warm, slightly acidified water, together with some pieces of the membrane of a calf's stomach. The pepsin in presence of the dilute acid dissolves the albumin, and the colouring matters as chrome-green, lamp-black, chrome-yellow, ultramarine, ochre, &c., are now readily removed by washing. Pepsin can bring about the solution of albumin coagulated by boiling, as well as that of otherwise insoluble albumin, but the two solutions differ, as the former will not coagulate on boiling, but the latter will. The presence of a small quantity of free hydrochloric acid is indispensable in aiding the solution of the albumin by the pepsin. Dilute hydrochloric acid (1 part of sp. gr. 1·169, in 100 of water) alone, after some days, at a temperature of 38°, can effect the solution of insoluble albumin. The solution will coagulate on boiling, and answers well in printing. By digesting blood-fibrin in dilute hydrochloric acid, a fibrin solution is obtained, which coagulates on boiling, exactly as the albumin solution above mentioned does. It is thus possible that fibrin would make a good substitute for egg-albumin. Coagulated fibrin, like albumin, on treatment with acidified pepsin-solution, dissolves, but apparently in an altered or modified form, as the solution will not coagulate on boiling. Coagulated fibrin can also be dissolved gradually, by dilute hydrochloric acid (1 part of sp. gr., 1·169 to 100 of water). On heating, the solution precipitates the fibrin as a thick, solid jelly.

W. S.

**Cellulose Manufacture.** By M. Faudel (Dingl. polyt. J., ccxix, 428—436).

Wood is heated with caustic soda-ley, of 8° to 12° (Beaumé), in iron vessels, at a pressure of 10—14 atmospheres; the undissolved mass is washed, and reduced to pulp, and is then extremely well adapted for paper-making. The drawbacks to the process are (1) the loss of soda (the brown liquor from the wood is boiled down and strongly heated) and consumption of fuel; and (2) the destruction of the iron vessels.

M. M. P. M.

**Effects produced on Cotton Fabrics by Ozone and Frost.** By F. Goppelsröder (Dingl. polyt. J., ccxix, 540—544).

Köchlin observed during the winter months that cotton fabrics which had been dyed with indigo perceptibly lost their colour, if, instead of being dried, they were laid aside in the factory in a damp condition, and exposed to the frost.

Since the cotton was exposed only to air and moisture, this decolorisation must have been produced by the action of one or both of these agents; the author therefore submitted a number of similarly dyed pieces of calico to the action of the different constituents of the atmosphere separately, and in this way succeeded in tracing it principally to the action of atmospheric ozone. The crystallisation of the water in freezing has, however, also a certain action upon the colouring matter, as well as upon the fibre.

Pieces of calico dyed with other colouring matters were subjected

in a similar way to the action of moisture and ozonised air, and in most cases the result was the same, viz., either a change in colour, or a more or less complete decolorisation. It is suggested to employ ozonised air for the rapid development of certain colours, as for example, aniline black, the fibre of the material being in no way injured by the treatment.

H. H. B. S.

## Emulsion Collodion and the Influence of different Bromides.

By L. WARNERKE (Phot. Jour., xvi, 144—148).

THE author describes his mode of preparing from gelatinised cotton a pyroxylin which furnishes emulsion collodion having very excellent properties. From raw hemp, he has also prepared a pyroxylin in some respects similar; but in Whatman's hand-made papers, he finds ready gelatinised cellulose in every way suitable for the purpose.

Experiments to determine the effects of different bromides in the emulsion showed that these vary with the nature of the salt employed. Thus, of all those tried by the author, he found that the zinc emulsion for negatives far surpassed the rest in every respect; potassium, though less sensitive, possessed some compensatory good qualities; while cadmium preparation showed the greatest tendency to fog. The photographic properties of a collodion are, therefore, powerfully affected by the nature of the metallic basis of the haloïd salt employed.

R. R.

## Photographic Action of Eosin.

By J. WATERHOUSE (Photographic Journal, xvi, 135—136).

WITH the new red dye, known by the name of eosin, the author obtained results similar to those which Vogel has described for other colouring matters. The action in the yellow and green part of the spectrum was very strong; but upon trying in the camera plates prepared with the tinted collodion, it was found that the time required for exposure was increased threefold; and although the images of the foliage and other green and yellow parts of the landscape were denser and clearer in the shadows, there was no gain in the matter of detail; and but little practical advantage was obtained by the use of the stained collodion.

R. R.

## Use of Photography in Printing Textile Fabrics.

(Dingl. polyt. J., ccxx, 192.)

IN England, the light of the sun has, for a long time, been used as a means of producing certain colorific changes upon prepared materials, and in this way different print-patterns have been produced of marvellous effect.

Potassium bichromate is extraordinarily sensitive to light. If a piece of cloth saturated with this salt be placed behind the Venetian

blinds of a window, so that alternate light and dark bands fall upon it, it will be found to be peculiarly coloured where the light has fallen. This principle is turned to practical account as follows:—

A piece of paper or thin plate of metal, with the pattern cut out upon it, is laid on the fabric, which has been previously saturated with the bichromate solution. Both are now enclosed in a frame, in which they are pressed together, and the frame, with the paper or plate exposed, is set in diffused light. An exact copy of the pattern coloured in a very remarkable manner is thus produced. The tint is a pale red. This colour will act as a mordant with madder, logwood, fustic, &c. Thus the fabric, with its pattern already fixed in the above manner, is placed in a bath of the above colouring matters, when the pattern alters its tint by appropriation of some of the colouring matter of the bath. If a fern-leaf be placed on a glass plate, with a piece of prepared stuff stretched behind it, all the exposed parts in the light become coloured, whilst the parts protected from the light by the fern-leaf remain white. Thus a white fern-leaf on a pale red ground is obtained.

W. S.

## Resorcin-black. By R. Wagner

(Deutsche Industrie Zeitung, 1876, 4; Dingl. polyt. J., ccxx, 96).

Resorcin obtained on a large scale by fusing disulphobenzoic acid with potash, when brought into contact with certain reagents, shows remarkable colorations, which seem to prove that it it is not merely of interest as a final product of the preparation of fluorescein and eosin. An aqueous solution of resorcin, treated with copper sulphate and sufficient ammonia to redissolve the precipitate formed, gives a deep black solution, which dyes wool and silk black, and may be used also as ink.

D. B.

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## Madder-red transformed into Orange. By Ch. Strobel

(Dingl. polyt. J., ccxx, 351).

By placing cotton articles dyed with aniline colours in a wooden vessel, and exposing them to the action of vapours of nitric acid, these colours are destroyed like indigo-blue. Steam-green and steam-blue gain when treated in the same manner in brightness of colour, and madder becomes converted into a beautiful orange colour, which cannot be reconverted into the original red colour by boiling it with soap-solution. If the action of the acid is not carried on long enough (at least 4—5 minutes) an orange is obtained, which goes over into a brown, if treated with dilute alkalis or soap-solution.

This paper is well worthy of notice, as it shows the existence of an independent and perfectly stable madder orange, the direct manufacture of which will soon be looked for—in fact seems to have been commenced, in so far as several German alizarin manufacturers are offering to dye-works a beautiful bright alizarin-orange.

D. B.

## A Means of protecting Alizarin from the Action of Iron.

By J. WAGNER and J. DEPIERRE (Dingl. polyt. J., ccxx, 349—350).

IN printing on cotton with alizarin, it is very difficult to prevent the steel of the apparatus from acting on the colouring matter. In some cases brass (if suitable) is used instead of steel, or the latter is coated with shellac, or a mixture of wax and soap, in order to protect the colour from direct contact with the metallic iron. This, however, is very troublesome, and not always convenient. Wagner recommends to add potassium sulphocyanate (20 g. to 1 litre) to the colour. Depierre found that this salt was active only when the mordant of alumina was in the form of nitrate, and not as acetate, because the iron has to be oxidised to sesquioxide before the potassium salt will act. The ammonium salt does not answer. Salts of arsenious acid seem to be the cheapest means of protecting alizarin from the action of iron; they form ferric arsenate, which is not capable of forming with alizarin a lake that can be fixed upon cotton. The contamination of the printed cotton with iron is thus prevented, and only the pure alumina lake, that is to say, the pure alizarin-red, remains upon the cotton.

D. B.

## A New Method of Dyeing with Artificial Alizarin.

By R. FORSTER (Dingl. polyt. J., ccxix, 539—540).

THE usual method adopted in dyeing Turkey red consists in subjecting the fabric firstly to the process of oiling; secondly, to treatment with alumina; and lastly, to the action of the colouring matter. By the new method the first and last operations are performed simultaneously. The alizarin is dissolved with soap in the requisite quantity of water, and the solution neutralised with sulphuric acid. A mixture of alizarin and fatty acid becomes thus separated, furnishing permanent and very brilliant colours.

H. H. B. S.

## Chemical Manufacture of Paper from Wood.

By C. M. ROSENHAIN (Dingl. polyt. J., ccxx, 81—87).

WOOD yields two products, very important in the manufacture of paper: (1) the so-called mechanical wood-tissue obtained by grinding wood; (2) the cellular tissue, so called wood-cellulose, obtained by the action of chemical agents on wood. The former does not form so good a substitute for rags as the latter, which yields a substance of striking compactness, from which the best qualities of paper can be produced.

In 1865 a large paper factory, belonging to Jesop and Moore, at Manayunk, near Philadelphia, established a wood-cellulose factory, and based their method of working on the experiments of Ch. Watt and H. Burgess. Owing to the want of machinery and apparatus, the quality and price of the product did not come up to the requirements; however, these difficulties were soon removed, and in 1868 a

Gloucestershire paper company, in Cone Mills, near Sydney, erected large cellulose and paper works, and prepared their paper exclusively from cellulose, without the addition of rags. In 1871 an English and Swedish company started five large works in Sweden. Germany at the present time possesses six large factories, in all of which the above-mentioned method is used.

For the preparation of cellulose the wood of pine and fir-trees is the most profitable; the wood of oak trees, absolutely useless. After removing the bark, the wood is cut into small pieces about 20 mm. long, 10 mm. wide, and 5 to 8 mm. thick, after which they are passed through a machine similar to a large coffee mill. The cutting machine consists of a horizontal spindle worked by steam, having at one end a centrifugal wheel with cutter (Müller's wood-cutting machine, *Dingl. polyt. J.*, ccxv, 399).

The wood is then brought into perforated leaden vessels, which are wheeled into a horizontal boiler. After having filled the boiler, it is well closed, filled with caustic soda, and heated by a fire. (Clarke's Boiler, *ibid.*, clxxi, 196; Keegan's Method, *ibid.*, ccviii, 316.) After four hour's boiling (the pressure corresponding to ten atmospheres) the boiler is emptied. The residue, consisting of cellulose, is well washed, then bleached, dried and cut into sizes suitable for packing. The liquor from the boiler is evaporated and again worked up for soda (Fraudel, *ibid.*, ccxix, 428).

On account of its toughness, cellulose is used only for the preparation of good qualities of paper, in its unbleached condition for the preparation of brown or grey paper, and bleached for the preparation of white paper as a substitute for white linen. The minimum market price of dry and unbleached cellulose is 22·5, and of bleached 31·5 marks, and, according to a trustworthy paper manufacturer, cellulose at present, if worked up for paper, gives for every 50 kilos. of paper produced a profit of at least 6 marks more, as compared with that of paper made from rags. 100 kilos. of dry cellulose give a net profit of about 12 marks, corresponding to a gain of 25 per cent. on the capital invested. Dry cellulose can be manufactured anywhere, moist cellulose (containing from 60—70 per cent. of water), however, only at places not very far from paper-works; places near the river are the most suitable. The water, which, although not pure, must be clear, ought to be sufficient to supply about 2 cm. per minute. 100 kilos. of cellulose require 400 kilos. of wood, 28 kilos. of caustic soda, and about 350 kilos. of coal. For the production of 20 tons of cellulose per week, about 55—65 workmen are needed, and, besides the above substances, also 5 tons of lime.

The greatest demand for cellulose is found in Germany, and in Austria and Hungary. In England, the better qualities of paper still fetch prices high enough to allow manufacturers to use rags for paper-making. Cellulose is also used on the Continent as a substitute of felt for inner soles of shoes, also as a substitue of india-rubber rings for tight joints. In conclusion, the author states that Germany at present produces yearly about 250,000 tons of paper, and Austria about 100,000 tons; and by supposing that only one-fifth of this quantity be made from cellulose, this alone would require a yearly

production of 70,000 tons of cellulose, or 280,000 tons of wood, showing that the production of this article will become of great importance in these countries.

D. B.

**Gentian Violet.** (Chem. Centr., 1875, 511—512.)—This new aniline-violet, which is considerably cheaper than the methyl violets, occurs in commerce in three shades, B, blue; BR, medium; and R, red. The dye is dissolved in 30 times its weight of water at 60°, brought to the boil quickly, and filtered. A bath for 5 kilos. of wool requires 200 grams of tartar, the requisite quantity of colour is added, the whole boiled and skimmed previous to passing the yarn, which should be done three times. The dye takes on equally.

C. E. G.

**A "forgotten" Colour for Glazed Leather.** (Dingl. polyt. J., ccxix, 93.)—The simple decoction of onion-peel communicates to glazed leather a very beautiful orange-yellow. As a mixing colour with the bright bark colours, especially willow bark, it furnishes the most delicate light tints, adding also a particular gloss and fire. Used as a yellow pigment for all brown shades, these are rendered brighter and more expressive. It also seizes readily upon those leathers which are difficult to colour, and covers them well and equally.

W. S.

**Indelible Ink for Printing Cotton and Linen Fabrics intended for Chlorine Bleaching.** (Chem. Centr., 1875, 576.)—One part of coal-tar is to be mixed with one part of benzene and one-tenth part of lampblack. The mixture can be made thinner or thicker by using more or less benzol.

H. H. B. S.

**Painting with Water-glass.** (Dingl. polyt. J., ccxix, 373.)—The surface (wood, brickwork, or metallic) must be dry, and free from rust, or any kind of fatty matter. Any of the pure mineral colours may be used. Powdered lime, or heavy spar amounting to 20—25 per cent. by volume is mixed with the colouring matter, and double as much water-glass is added.

M. M. P. M.

**White Barrel Soap.** (Dingl. polyt. J., ccxix, 374.)—This substance, which answers its purpose well, may be made by mixing 1 part of warm cocoa soap, containing 73 per cent. of fatty acids, with 30 parts of water-glass solution of 37½ per cent. Baumé.

M. M. P. M.

**Sugar Colouring Matter.** (Dingl. polyt. J., ccxix, 374.)—100 kilos. starch sugar are heated with 1·75 kilos. caustic soda, or with 3·25 kilos. of soda crystals, whereby a colouring matter suitable for liqueurs, &c., is obtained.

M. M. P. M.

# PAPERS READ BEFORE THE CHEMICAL SOCIETY.

## X.—*On Variations in the Critical Point of Carbon Dioxide in Minerals, and Deductions from these and other Facts.*

By W. N. HARTLEY, King's College, London.

SINCE the publication of my former paper on this subject, I have, through the kindness of several gentlemen, had the opportunity of multiplying my observations, and I now propose to lay some of the results before the Society. Before entering upon these, however, I desire to refer to a paper of the late Mr. Alexander Bryson, published in the *Proceedings of the Royal Society of Edinburgh*, in 1860—61. It was the result of ten years' work, comprising an examination of microscopical sections of various rocks. Fluid cavities were noticed in many specimens of granite, the gas bubbles in which disappeared when warmed on a hot stage to 35° C., and returned on cooling to 29°, the liquid undergoing at the same time what appeared to be a sort of boiling movement. Not knowing the nature of this liquid, Bryson concluded that granite was crystallised from aqueous solutions at a temperature not exceeding 29° C. He remarked the same liquid in hexagonal prisms of quartz, in porphyry from Dun Dhu in Arran, in the schorl of Aberdeen granite, and also in the trap tufa of the Calton Hill, the basalt of Samson's Ribs, and greenstone from the Crags in the Queen's Park, Edinburgh. I conclude that this liquid is carbon dioxide, for if we take the mean of the two temperatures quoted, we obtain 32° C., which is very near the true critical point of that liquid.

In the paper of Messrs. Sorby and Butler, referred to on a former occasion (*Proc. Roy. Soc.*, 1869), there was no mention of this seeming ebullition, and this was one of the reasons why I doubted the justness of their conclusions. In a later publication (*Monthly Microscopical Journal*, vol. i, p. 222) Messrs. Sorby and Butler say with regard to the liquid in sapphires, "After having been warmed, so as to expand and fill the cavities, the liquid on cooling often suddenly boils violently; and when these phenomena are observed under the microscope they are extremely curious and interesting." It does not seem in either case to have been clearly ascertained that the substance was in the Cagnard de la Tour state.

The curious appearance of ebullition I have studied very attentively. When the heated gas is chilled, a mist forms throughout the

cavity, without being disturbed by gravitation. The individual spherules of this mist grow so large that they begin to touch each other, to coalesce, and to gravitate. They of course at the same time entangle gas, and as they descend to the lower part of the cavity the spherules of gas or bubbles take an opposite direction; consequently when a portion of the liquid has collected at the lower end and gas at the upper, there are showers of liquid descending into, and streams of bubbles rising out of the liquid. In two or three seconds the movements cease.

In Figs. 1 and 2 are given representations of a fluid cavity in a topaz belonging to Mr. James Bryson, of Edinburgh, to whom I am indebted for allowing me to examine some of his valuable specimens. When at a temperature two or three degrees below the critical point, the liquid has the appearance seen in Fig. 1, but when it is further heated, there is no line of demarcation in the centre of the cavity; the effect of sudden cooling is seen in Fig. 2. The *spherules* called *gas* and *liquid* are passing in the direction of the arrows nearest them. In Fig. 3 is shown a smaller cavity of a similar character seen in rock crystal. The conditions of this boiling seem to be that the liquid carbon dioxide shall be equal in volume to the gaseous portion at ordinary temperatures, and that the cooling down from the state of gas shall be sudden.

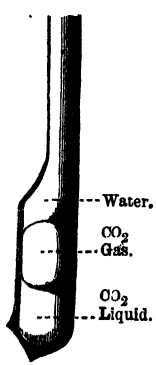


FIG. 1.

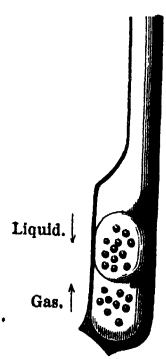


FIG. 2.

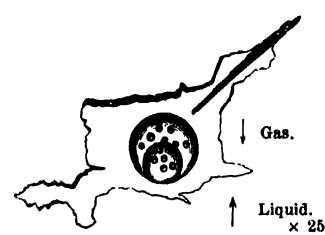


FIG. 3.

When the liquid collects, at first the curvature and the boundary line in contact with the gas are slight and indistinct, but as it increases in quantity so does the curvature increase. The appearances, in fact, are like those seen at a higher temperature in Prof. Andrew's tubes of sulphur dioxide.

The account of experiments made by Vogelsang and Geissler (*Pogg. Ann der Physik*, 1869, cxxxvii, 56) on the liquid enclosures in minerals, shows that they tried the effect of heat on the liquids, but

found some difficulty in ascertaining the temperature at which the bubbles disappeared; they, however, concluded it to be 32° C.

In addition to their experiments with vacuum tubes and the spectroscope, they broke quartz containing the fluid under baryta water, and got a distinct turbidity produced. They remarked the rate of expansion of the liquid by heat, but in a less satisfactory manner than Messrs. Sorby and Butler.

The most exact evidence of the nature of the expansible fluid which places beyond doubt the fact of its being carbon dioxide, is the following:—

The recognition of the spectrum produced by the electric spark in a tube which contained such gas only as was liberated by the decrepitation of the minerals, and the turbidity caused by crushing quartz under baryta-water. (Vogelsang and Geissler, 1869.)

The rate of expansion of the liquid in sapphire, very accurately measured and compared with that of carbon dioxide and other liquefied gases. (Sorby and Butler, 1869.)

The accurate determinations of the critical point made by myself in 1875—76, and compared with the true critical point of carbon dioxide.

To ascertain the critical point, it is necessary to observe what high and low temperatures the liquid and gaseous states of the substance respectively can withstand. For this purpose three little thermometers were used, two of which were made expressly for me by Mr. Casella. They are each 2½ inches in length; one has a range of − 20° to 140° F., the other two are made to register tenths of a degree centigrade between 25° and 33°. When the cavities cannot be seen with a 1-inch or 2-inch objective, but when a ½-inch or ¼-inch is available, the simple method I have already described in my former paper fulfils this purpose admirably if skilfully performed. I say this after having tried every conceivable method.

One form of apparatus was a water-tight cell into which the bulb of a thermometer was fixed, and through which a stream of water flowed as through a Liebig's condenser, the whole being clamped to the microscope stage. The refinement on my original plan, which gives one more confidence in the results, consists in placing the mineral in a glass trough beside one of the small thermometers; the whole is then immersed in water at a suitable temperature, and after being stirred round twice or thrice is left for five minutes. It is then removed with water in it; the sides of the trough are wiped dry, and it is placed on the microscope stage; but in order to separate it from the metal by a non-conductor of heat, two india-rubber bands are placed round it. A good lens is so arranged near the thermometer that the cavity may be observed through the microscope with one eye and the thermometer be read *simultaneously* through the lens with the other. When the cavities are

so small that only a $\frac{1}{2}$ or a $\frac{1}{4}$-inch objective can be used, the original method of examination must be resorted to, as the working distance prevents the possibility of using a glass trough. An exceedingly useful little contrivance consists of a glass tube about $\frac{3}{8}$ of an inch in diameter and 12 inches long; it is drawn out to a jet at one end of about $\frac{1}{16}$ of an inch aperture, the jet being bent at an obtuse angle at about an inch from the point. To prevent the glass being softened and bending when heated, it is covered for 4 inches in its central part by a piece of brass tube, which just slides on not too easily. The straight end of the tube is somewhat pointed, and passes through an india-rubber cork fitting into a universal joint upon a stand having a sliding motion in the upright, so that it may be raised and lowered at will. The end of the glass tube which passes through the cork has a piece of india-rubber tube slipped over it, 15 inches in length, and connected with a ball syringe, whereby air may be drawn in and discharged again. By heating the metal tube with a spirit-lamp or Bunsen burner, the air discharged by squeezing the ball syringe will be heated, and may be directed on to the object while under the microscope without any displacement.* I have thus examined the specimens of quartz, B and C, described in my previous paper as containing nothing but water cavities, and have detected many cavities of very small size containing a small quantity of carbon dioxide floating on the water. Some of these cavities, in which the liquid was easily seen, were no larger than $\frac{1}{1700}$ of an inch in their greatest diameter, and the carbon dioxide was so small in quantity that it would have been unobserved had it not been for the instantaneous change in appearance of the contents of the cavity caused by warm air. Portions of liquid carbon dioxide so small as not to be recognizable under a magnifying power of 800 diameters, have been revealed by this heating tube. They could not have been greater than the $\frac{1}{50000}$ of an inch in diameter. I imagined that by using the polariscope in conjunction with the jet of warmed air, such a strain would be caused by the enormously increased pressure (equal to 109 atmospheres) that it would affect the polarizing power of the mineral, and by a display of colour make this visible even in very small cavities. Such is, however, not the case, though in large cavities the strain is seen, and the experiment is a very interesting one.

Mr. James Bryson, of Edinburgh, lent me some beautiful specimens of minerals with large fluid-cavities in them. These are fully described as follows:—

* On mentioning this to Mr. Butler, he showed me an apparatus which he contrived in order to show the boiling motion in one of his large specimens. The construction is that of a small metal wash-bottle heated by a lamp. To the blowing-tube is fixed a flexible pipe and an ivory mouth-piece.

No. 1. Barium sulphate. Twenty-nine large cavities were seen to contain a liquid and a bubble, the bubbles were unaffected by heat. Size of largest cavity, $\frac{1}{18} \times \frac{1}{26}$ of an inch.

No. 2. A beautiful specimen of barium sulphate, with a long cavity, measuring $\frac{1}{10} \times \frac{1}{32}$ of an inch. The contained liquid was water only.

No. 3. Barium sulphate, containing an immense number of small water cavities and a few of greater size, one measuring $\frac{1}{17} \times \frac{1}{30}$ of an inch.

No. 4. Barium sulphate. Many cavities containing water only, the largest measured $\frac{1}{10} \times \frac{1}{33}$ of an inch.

No. 5. Colourless rock crystal from Quebec. It contained a long pear-shaped cavity, partially filled with a brown viscid liquid. The viscosity seemed to be diminished by warming. The extreme length of the cavity was nearly half an inch and its breadth about $\frac{3}{10}$ths. The brown fluid is probably mineral naphtha.

No. 7. A topaz filled with oval fluid cavities. In only very few cases could the presence of two liquids be discerned, but the effect of heat showed that the liquid in greatest abundance was carbon dioxide.

*Variations in the Critical Point of Natural Carbon Dioxide.*

In examining the critical temperature of the liquid in this specimen of topaz just referred to, the following observations were made. Each number represents a separate experiment.

Temperatures at which the liquid was in the gaseous state—

| | |
|---|---|
| 30·9° C. | 29·8° |
| 30·9° | 29·5° |
| 30·8° | 29·1° |
| 30·5° | 28·6° |
| 30·2° | 28·8° |
| 29·5° | 28·2° |
| 29·5° | |

At 27·9° and 28° it was liquid. The critical point, therefore, seems to lie at or about 28° C. Fifteen other experiments showed it to be below 28·5°. There was some doubt whether the determinations were correct, on account of the difficulty experienced in knowing for certain whether the cavities were filled with gas or liquid, because the carbon dioxide easily filled the cavities by expansion before the critical point was reached, and it was not easy to say whether formation of a bubble was caused by the simple contraction of the liquid, or by the conversion of the carbon dioxide from the gaseous to the liquid state. It is true that the bubbles in forming (the microscope being inclined) moved across and sometimes around the cavities, showing that the

latter was the true cause of the return of the bubble, for had it not been so, the bubble would have re-appeared at the spot where it was seen to vanish. But the conclusion was open to some suspicion because the bubbles always came from the same ends of the cavities. I was, therefore, glad when I found the cavity, Fig. 1, containing water and a considerably larger proportion of gas than was seen in the others. As the liquid in this particular case always condensed with the remarkable boiling motion already mentioned, it was certain that it had attained the gaseous state, and as the carbon dioxide never expanded to such an extent as to fill the cavity entirely, there was no difficulty in ascertaining what temperature it could withstand. The following numbers represent the readings of the thermometer :—

| Gaseous state. | |
|---|---|
| 29·5° | 28·7° |
| 29·2° | 28·6° |
| 28·9° | |
| 28·8° | |

There is no mistake about these numbers; the critical point is 28·5°

On another occasion, a further series of experiments was made with the following result. In the cavity, which was only half full of liquid, Fig. 1, it appeared that the carbon dioxide had a higher critical point than that in the other cavities containing a much greater proportion of the liquid—thus at the temperatures 27·65°, 27·5° and 27·25° the carbon dioxide apparently existed as gas in all cavities excepting that shown in Fig. 1, and the bubbles did not return till the temperature had sunk to 26·6°, 26·5°, 26·5°. As in these cases the bubbles travelled, it seemed to be a true *condensation* and not merely a *contraction* which caused its return. I am, however, inclined to think that though the liquid is formed probably at 28·5° in all the cavities, yet it requires a very considerable amount of contraction before its liquid volume shall be less than that of the cavity. I mean that when the liquid is formed it is in a state of great compression, and that a considerable amount of contraction is required to remove this compression. Furthermore, after the compressed state of the liquid is relieved, that a further contraction is required to tear the liquid away from the moist walls of the cavity. Although I have expressed the opinion that the liquid, when simply expanded so as to fill the cavity by expansion, always contracts, so that the bubble returns at the same spot where it was last seen, yet I cannot think that this is exactly true in cases where the expansion is sufficient to fill the cavity at a temperature two or three degrees below that of the critical point.

In the foregoing experiments, the specimen was examined while immersed in a trough of water, but it was considered advisable to put

it in water at the following temperatures, remove, hastily dry and examine it. Observations of the long cavity, Fig. 1, thus made, showed that at 28·4°—28·3°—28·1°—28·1°, the carbon dioxide was in the gaseous state, while at 28° it was seen to be liquid.

My friend, Mr. B. L. F. Potts, of Camberwell-grove, lent me a beautiful twin crystal of colourless topaz. A large shallow cavity was noticed, containing very little liquid carbon dioxide floating on water, and a large proportion of gas. From five experiments the critical point was ascertained to lie between 26·5° and 28°; from the shape of the specimen it was difficult to examine it more satisfactorily.

Specimen of quartz. Cavity not easily seen. Gas at 31°. Liquid at 30·9°—30·9°. This was a cut specimen, mounted for the microscope.

Specimen of Topaz. Colourless, obtained from Mr. Darker. The liquid was easily made to fill the cavities by expansion, and therefore it may be doubted whether these temperatures will yield the true critical points.

The carbon dioxide was gaseous at 27·7°, 27·7°, 27·7°, 27·7°, 27·6°, and liquid at 27·0°, 27·0°, 27·2°, 27·4°, 27·5°.

Critical point between 27·5° and 27·6°.

Cut specimen of Tourmaline from North America. Cavities containing water and carbon dioxide—the cavities were not inconveniently full. The following temperatures each represent a separate experiment:—

| Gas. | Liquid. | |
|---|---|---|
| | 26·9° | |
| 28° | 26·6° | Plainly visible. |
| 27·9° | 26·75° | Seen with difficulty. |
| 27·7° | 26·75° | |
| 27·5° | 27·25° | |
| 27·4° | 27·25° | |
| 27·3° | Boiling seen on cooling to just below this temperature. | |
| | Critical point 27·27°. | |

In each experiment the substance was placed in water of the temperature stated.

Tourmaline from North America. Cavities contained both water and carbon dioxide; it was in the gaseous state at 27·2°—27°, and the liquid was seen to be returning at 26·95°—26·9°—26·9°; it was plainly seen at 26·8°, and on cooling below this temperature the liquid contracted. The cavities contained sufficient liquid to expand or contract with increase and decrease of temperature, but not sufficient to fill the cavities, the critical point was, therefore, easily determined. These two specimens were lent me by Mr. Potts.

Specimen of quartz, cavity with water and carbon dioxide, the latter seen only with a half-inch objective—

| | | | | |
|---|---|---|---|---|
| Gas at ..... | 31·0° | 31·0° | | |
| Liquid at..... | 30·5° | 30·7° | 30·9° | 30·9° |

The trough could not be used in this case, so that the specimen had to be removed from the water, wiped hastily, and placed on the microscope stage; in operating in this way, $\frac{1}{10}$th of a degree is as near as the extremes of gas and liquid can be approached.

A specimen of quartz. Lent by Mr. W. G. Lettsom. The cavity was well seen with a half-inch objective. It contained water and liquid carbon dioxide,—the latter in sufficient quantity to fill the cavity by expansion. The following temperatures were taken:—

| Liquid. | Gas. | |
|---|---|---|
| 30·9° | 32·9° | |
| 30·8° | 32·6° | |
| 32·0° | 32·5° | The liquid state returned instantly. |
| 32·0° | 32·5° | |
| 32·2° | 32·5° | |
| 32·4° | | |

Critical point about 32·5°.

This temperature is not sufficiently wide of the critical point of carbon dioxide to justify any suspicion of the liquid being any other substance, and as the specimen was a microscopic section of quartz, there is no likelihood of error in taking the temperature to account for this variation. As the half-inch objective had to be used, the method of taking the critical point was the same as that employed for the tourmalines, which show a variation in the opposite direction.

Another specimen of quartz. From Mr. Lettsom. One cavity containing water and sufficient carbon dioxide to fill the cavity by expansion:—

| Liquid. | Gas. | |
|---|---|---|
| 32° | 35° | |
| 32·5° | 34·75° | |
| 32·7° | 34·5° | |
| 32·9° | 34·0° | |
| 33·0° | 33·7° | Liquid instantly returned. |
| 33·0° | 33·7° | |
| 33·0° | | |
| 33·6° | | |
| 33·6° | | |

Critical point 33·7°

Another similar cavity was observed in the same specimen, but was too small to make any trustworthy experiments with.

A third specimen of quartz, also belonging to Mr. Lettsom. The cavities all contained water, and, in addition, carbon dioxide as liquid. The specimen was cut and mounted for the microscope, and the cavities were examined with a two-inch power.

| Liquid. | Gas. |
|---|---|
| 28·5° | 29·6° |
| 28·8° | 29·5° |
| 28·8° | 29·4° |
| 29·0° | 29·2° |
| 29·0° | 29·0° liquid reappeared. |

Critical point 29°.

The liquid could expand so as to fill the cavity; the specimen, therefore, was inverted, and as the bubble re-appeared at a fresh place, it was considered that the critical temperature had been reached. Another larger cavity in the same specimen was liquid at 30·9° – 30·9°, and gas at 31°. Hence two cavities in the same specimen may contain liquids with different critical points. About twenty tourmalines, four sapphires, several topazes from Brazil, and two or three beryls from Ceylon, yielded nothing of interest. About two dozen garnets of different kinds were examined; no cavities were seen, but they invariably contained crystals of what appeared to be spinel.

*Examination of Rock Sections.*

Professor N. S. Maskelyne placed a microscope at my disposal in the British Museum with a large number of rock sections of great interest. Of these thirty-six specimens were chiefly trachytes from Hungary. Many of these had cavities in them containing fluids, generally water. One piece of grey trachyte from Ober Fernezely, Hungary, had a few cavities containing two fluids. There were five hypersthenites from Bohemia, a piece of serpentine and one of hornblende slate from Baden. Five specimens of syenitic granite from the Isles of Mull and Skye, and diorite from Arran contained minute water cavities; one of the specimens from Mull seemed to be worth a second examination. Four specimens of diabase from Kinghorn in Fifeshire and one from the Cuchullins in Skye. Three specimens consisting of felsite, felstone, and greenstone from Mull. A piece of quartz porphyry from Sligachan in Skye. Porphyritic pitch-stones from the Isles of Arran, Eigg, and Mull, and twenty-four various rocks from different sources, many of these were basalts, in all eighty-seven specimens. Trachytes, porphyry, sanidine rock from the Laacher See, diabase

from Norway and Nassau. Trachyte from the Siebengeberge and from Klinikler Thal in Hungary to the number of thirty-seven specimens were also examined. The following were from Professor Maskelyne's own collection:—Four sections of Aberdeen granite, syenitic granite from Mull and Skye, two sections of trap tufa and two of green jade, twenty-one specimens of Labrador felspar from Lake Baikal, and porphyry from Greenland, felstone from Mull, two basalts from Auvergne, from the Cave Hill Belfast, the Giant's Causeway, and Unkel on the Rhine, Dutzbach, and Frankfort contained nothing leading one to a more detailed examination. A rock from Thjorsa in Iceland, consisting of anorthite, augite, and olivine, contained some small cavities apparently holding two liquids. Eulysite from Sweden, which consists of augite, garnet, and olivine, and enstatite from the Haute Loire contained no cavities.

These notes indicate the particular direction of inquiry which may possibly lead to interesting facts, and which will be continued. According to the regulations of the British Museum it was impossible to make use of the heating tube for these specimens.

From the collection in the British Museum the following minerals were examined, namely, three emeralds:—

No. 1. A small specimen from Santa Fe de Bogota, water cavities only were seen.

No. 2. A large specimen from the same locality contained a large number of cavities, within which was an aqueous solution. In every case there was seen a bubble, and beside it a square crystal of about twice the size of the bubble. Similar bubbles and crystals have been seen by Messrs. Sorby and Butler in emeralds (see *Proc. Roy. Soc.*, vol. xvii, pl. vii, fig 8).

No. 3. A large specimen as before. Water cavities only were noticed.

No. 4. A cloudy beryl from Surat, Bay of Cambay, India Contained water cavities.

No. 5. Another beryl from Surat contained an immense number of cavities, some containing two fluids. Experiments made on the critical point by immersion in a glass trough.

The substance was liquid at 30·8°, 30·9°, 30·9° C., it was found to be gas at 31°, 30·95°, 30·95°; the difference between these latter observations shows the critical point to be about 30·92°.

At 30·9° the liquid had almost entirely filled up many of the cavities, only a small bubble was seen; on cooling even two- or three-tenths of a degree the liquid contracted to a wonderful extent. Boiling was seen in many cavities on cooling down from the critical temperature.

Zircons. No. 1. From Ceylon; many cavities perfectly dry and apparently empty.

No. 2. From Ceylon; contained curious rounded semi-opaque spots.

No. 3. Red Australian zircon. Nothing seen.

No. 4. From Ceylon; contained nothing but opaque matter.

No. 5. Crystals of zircon from Ceylon; full of cavities but no liquid,

Olivine. No. 1. Fine crystal of olivine from the Levant; very irregular cavities, some apparently containing water and a bubble.

No. 2. A rough crystal; contained oval cavities apparently empty.

Twenty or thirty specimens of olivine in small crystals; nothing but opaque enclosures were noticed.

Oriental Sapphires. No. 1. This was a thick slice off a large crystal, it contained a little reddish colouring matter. It contained a great many small cavities and several very large ones with much carbon dioxide and very little water. This specimen was very thick, and there was some little difficulty in taking the exact critical point; it lay, however, between 30·5° and 31°.

No. 2. A smaller specimen filled with good sized cavities, containing much liquid carbon dioxide and but little water. At 26° it was expanded so as to fill the cavity, and at 25·5° the liquid returned suddenly.

No. 3. A cut specimen which had evidently been worn in a brooch; there were many cavities containing liquid carbon dioxide and a little water, the former was in the state of gas at a temperature of 30°; it became liquid again at 29·5°.

The following table shows all the variations noticed in the critical point of carbon dioxide existing in various minerals:—

| | Critical point. |
|---|---|
| Topaz | 28° C. |
| Topaz | 28° C. and 26·5° |
| Topaz | 27·55° |
| Tourmaline | 27·27° |
| Tourmaline | 26·9° |
| Sapphire | between 30·5° and 31° |
| Sapphire | between 25·5° and 26° |
| Sapphire | 29·5° |
| Rock crystal | 30·95° |
| Rock crystal | 30·95° |
| Rock crystal | 32·5° |
| Rock crystal | 33·7° |
| Rock crystal | 29° |
| Rock crystal | 30·95° |
| Beryl | 30·92° |

*Inferences as to the Formation of Corundum and Topaz.*

It is noticeable that sapphire and topaz both have the critical point of the carbonic anhydride they contain altered to the extent of two or three degrees below the normal temperature. This indicates the presence of some incondensable gas. Andrews (*Proc. Roy. Soc.*, 1875) has shown that the critical point is lowered considerably by traces of such gas. As nitrogen has been detected in the fluid cavities of quartz by Sir Humphry Davy, it is probable that the same gas is here present. It is inconceivable how the atmosphere can have penetrated to the bowels of the earth where these minerals were formed under great pressure; the possibility, indeed, of its being air is excluded;* but nitrogen often escapes in a pure state from mineral springs and fissures. The same lowering of the critical point is observable in all the cavities in the two tourmalines from North America. In some of the specimens of quartz, the reverse, a raising of the critical point, is noticeable. This cannot be due to vapour of water, for the vapour tension of carbon dioxide at 28·3° C. is 70·39 atmospheres, and that of water at so low a temperature as 31° C., and so high a pressure as 70 atmospheres, would be practically *nil*. Again, we do not find it in any way affect the critical point in most specimens of quartz, therefore I believe the alteration to be due most probably to presence of hydrochloric acid. This gas has been recognised in the aqueous contents of cavities by Mr. Sorby (*Quarterly Journal Geolog. Soc.*, xiv, 453—500) and by myself. Its vapour tension at 10·6° when liquefied, according to Mitchell, is 40 atmospheres, while according to Davy and Faraday, that of carbon dioxide at the same temperature is 60 atmospheres. We may quite expect that a solution of the gas in water would affect the critical temperature of carbon dioxide in the same manner as, and perhaps more decidedly than the dry gas. As the specimens in which the high critical point was seen were not my own, I could not destroy them for the purpose of deciding this question. With regard to the formation of corundum and topaz, Hautefeuille has obtained the former artificially by passing nitrogen laden with water vapour and hydrofluoric acid over alumina in an intensely heated porcelain tube; the aluminium fluoride formed is decomposed, and crystals of corundum line the interior of the tube (*Ann. Chim. Phys.* [4], iv, 153). Now if aluminium fluoride or chloride were to come in contact with calcium carbonate, a decomposition would occur in which carbon dioxide and alumina would be separated. The former, being compressed, would form cavities for

* The small amount of air dissolved in water might possibly be retained while the percolation of soil and rocks continued, but it would not be liberated easily from its dissolved state.

itself in the crystals, and on cooling would liquefy. Were the aluminium fluoride or chloride in the state of vapour, or if the aluminic compound be cryolite, the resulting liquid carbon dioxide would be dry, and this in some of the specimens possessed by Mr. Butler appears to be the case. In topaz and some sapphires, however, water is present, but not in any considerable quantity, which points to the conclusion that in such cases the minerals were formed from moist materials, but not from aqueous solutions, as is the case with quartz and tourmalines.

As aluminium chloride boils at 180°—185° C., and as cryolite fuses below a red heat, it is obviously within the range of possibilities that one of these substances, or both of them in fact, may be sources of crystallised alumina when brought into contact with limestone in a heated state. It is remarkable that in those cavities where no water accompanies carbon dioxide, the liquid has no adhesion to the walls of the cavity, and therefore presents a surface to the gaseous portion, which is convex. Vogelsang and Geissler have likewise noticed that in some cases the liquid takes the same direction of curvature as mercury. It is undoubtedly the moist or dry condition which causes the greater or less adhesion, and consequently the concave or convex curvature.

In making these observations it is necessary to get rid of double refraction by fixing a Nicol's prism on to the microscope stage; otherwise in small water cavities the appearances are very similar to those seen when two liquids are present, so that one may be easily deceived.

### *A Theory of the Formation of Diamonds.*

The native matrix of the diamond in Brazil is a hydrated rock, itacolumite, which contains chlorite and talc. It is evident then, as Bischof has pointed out, that the substance itself cannot have had an igneous origin. It is impossible to say what temperature short of the critical point of water it may not have endured, for, under great pressures, hydrated rocks are not decomposed by heat. The experiments of Kemp, Silliman, Jacquelain, and Despretz all tend to disprove the origin of diamond through the agency of intense heat. Jameson considered the diamond to be of vegetable origin, and Liebig suggested that it was the final result of a gradual separation of the hydrogen, oxygen, and nitrogen from the carbon of organic substances by a slow process of decay, the intermediate products of which are hydrocarbons, such as naphthaline. But the researches of Pasteur have proved that the decay of organic matter is not a direct process of oxidation, as was formerly accepted solely on the authority of Gay-Lussac. Bischof (*Chemical Geology*, vol. i, p. 250, English edition) enters rather fully into reasons for believing that diamonds are formed only by aqueous

action, but not by decay alone. The fact of diamonds being found in association with brown iron ore in the Ural Mountains, and with hydrated ferric oxide of recent formation in Brazil, he believed to afford evidence of the dehydrogenation of organic matter by means of sulphates and ferric hydrate, which are reduced to sulphides and ferrous compounds. I am more inclined to attribute the formation of diamonds either to the reducing action of moist sulphides on highly compressed and moderately heated carbon dioxide or to the mutual reaction of hydrocarbons and carbon dioxide, whereby carbon may be separated and water formed, or the action may be a combination of both these processes. It is difficult to believe that diamonds are entirely formed by a process in which unoxidised forms of carbon are intermediate products, otherwise they would occur not unfrequently in the neighbourhood of coal formations. Let us consider what would be the effect of an enormous pressure of rock on carbon dioxide heated above its critical temperature: it would be in a condition, as far as we can tell at present, capable of unlimited compression, so that, taking into consideration the comparative incompressibility of water, it would be possible to convert it into a gas with a greater density than that of water. For instance, at 63·7° under a pressure of 223 atmospheres, the gas has been reduced to $\frac{1}{447}$ of its volume (Andrews "On the Physical Properties of Matter, &c.," *Proc. Roy. Soc.*, 1875). Under these circumstances it must be at least as dense, if not denser than water. There is no necessity to halt at this particular pressure, and the possibility of the chemical properties being altered even under these conditions presents itself to the mind. This theory, that diamonds are the product of reducing agents on very highly compressed carbon dioxide acted upon at temperatures above its critical point, which temperatures certainly do exist at inconsiderable depths below the earth's surface, at any rate introduces a new condition of things highly suggestive of further speculation, and, if possible, of experiment—conditions under which no chemical reactions have ever been made in the laboratory. To imitate the supposed operations of nature is difficult, because chemical reactions in the bowels of the earth are reactions carried on under tremendous pressures in sealed tubes of vast thickness.

To those gentlemen who have been so kind as to lend me specimens, I here return my best thanks. To Prof. Maskelyne, for his courtesy and kindness, I am particularly indebted. He placed a microscope, a working-room, and the minerals in the British Museum at my disposal, besides showing me every possible attention.

# XI.—COMMUNICATIONS FROM THE PATHOLOGICAL LABORATORY OF DR. THUDICHUM.

## No. III.—*On the Estimation of Hydrogen Occluded by Copper, with special reference to Organic Analyses.*

By J. L. W. THUDICHUM and HENRY W. HAKE.

IN 1843, Melsens, who assisted Dumas in his experiments on the Synthesis of Water, made the observation that when oxide of copper was reduced by hydrogen, the metal retained, in combination, some traces of this gas, and that the amount retained was greatest at a low temperature. Metallic copper, obtained from the oxide in some experiments on the synthesis of water, was subjected to a re-oxidation by perfectly dry air. In one case, 300 grms. oxide of copper yielded 0·065 grm. water; that is, 240 grms. of metallic copper had occluded 0·007 grm. hydrogen. In another experiment, in which Dumas asserts the temperature to have been as low as 175°, the amount of hydrogen occluded is estimated at 0·0002 grm. per grm. of copper, or nearly ten times as much as in the previously cited experiment (*Ann. Chim. Phys.* [3], viii, 1843, p. 205).

In 1866, Graham also estimated the hydrogen occluded by copper reduced from the oxide, by heating it in a vacuum and measuring the occluded gas. Graham states that 50 grms. reduced copper yielded 3·4 c.c. hydrogen. In another experiment which he made on copper wire, he found that 50 grms. had occluded 2·60 c.c. gas, of which 0·6 c.c. was principally carbonic oxide and the rest hydrogen (*Trans. Roy. Soc.*, 1866, p. 432). G. S. Johnson, in a recent communication to this Society, advanced the statement that a serious source of error in the determination of hydrogen in nitrogenous carbon compounds was due, and according to two experiments made by him might be traced back, to that property of copper by which this metal is capable of occluding hydrogen.

Johnson experimented upon 34·9 grms. of rolled copper-wire, and after oxidising this in the blowpipe flame, subjected it to a current of hydrogen at a red heat, leaving it to cool in an atmosphere of the same. Johnson then re-oxidised his copper wire by means of a current of dried air in the manner described by Dumas, and weighed the water formed. In one experiment, he obtains 0·02 grm. water, and in a second experiment with the identical roll of copper wire, 0·025 grm. (*Journ. Chem. Soc.*, clviii, p. 179). In the following table, the above results are made proportionate to 100 grms. of copper

each, so that the quantities of gas obtained may be compared absolutely—

| Copper used. | Form. | Hydrogen occluded. | Author. |
|---|---|---|---|
| 100 grms. | From oxide | 0·0029 grm. | Melsens. |
| 100 ,, | From oxide | 0·0200 ,, | Melsens. |
| 100 ,, | From oxide | 0·0006 ,, | Graham. |
| 100 ,, | Wire | 0·0003 ,, | Graham. |
| 100 ,, | Rolled wire | 0·0074 ,, (mean) | Johnson. |

The discrepancies of these results would prevent us from drawing any practical conclusion with regard to the influence of this phenomenon of occlusion upon hydrogen determinations, if we did not find an explanation in the varying conditions under which the experiments were made. Our principal object, therefore, in instituting the experiments about to be described was, by fixing the conditions of each event, to ascertain the actual error of excess in a single analysis consequent upon the presence of hydrogen not contained in the body analysed, but occluded by the copper-wire gauze used in the operation, and further to discover, if possible, a means of obviating all error arising from this cause. In these attempts we have been successful, as we shall now proceed to show.

*Experiment I.*—Six rolls of copper-wire gauze which had been used repeatedly for combustions in the laboratory, were once more oxidised at a red heat in a current of air, and subsequently reduced at a red heat and allowed to cool in a current of hydrogen as ordinarily done. About two hours after this operation, the six rolls, weighing 83 grms., averaging, therefore, 14 grms. each in weight, perfectly clean and bright to the eye, were introduced into a dry combustion-tube closed at one end. The tube was then drawn out at the open end, and after being placed on the combustion-furnace was connected with a Sprengel pump. As soon as the tube had been rendered vacuous, it was heated to bright redness for some 15 minutes, the gas then turned off, and the pump set working without removing the tiles from the top of the furnace. In a few minutes, a second vacuum was obtained, the hydrogen evolved being collected in a graduated tube over mercury. Here 83 grms. of copper-wire gauze gave 1·07 c.c. hydrogen normal, so that the error in the determination of hydrogen which would have been caused by the use of one of these rolls in a single combustion would have been that due to an excess of $\frac{1{\cdot}06 \text{ c.c.}}{6} = 0{\cdot}178$ c.c., or 0·0000159 grm. hydrogen.

On the assumption, therefore, that 0·4 grm. substance had been taken for analysis, the error in the percentage of hydrogen due to the

occlusion of that gas by the metallic copper used in the combustion would be 0·0039 per cent. excess.

*Experiment II.*—Perfectly new copper-wire gauze was cut into strips and rolled. Six rolls were again taken. These, after oxidation at a red heat in a current of air and subsequent reduction at a red heat, and cooling in a current of hydrogen, weighed 96 grms., averaging, therefore, 16 grms. each in weight. The amount of hydrogen occluded was estimated as described under Experiment I, with this difference, that the pump was set working as soon as a red heat was obtained, and the gas only turned off from the furnace as the second vacuum approached completion. This time, 96 grms. of copper gauze oxidised and reduced for the first time, gave 8·04 c.c. gas normal. On introduction of some caustic potash solution into the graduated tube, the total volume became 7·02 c.c., but no further absorption took place on introduction of pyrogallic acid. After closing the opening of the tube with a glass plate and inverting it, the plate was cautiously removed and a light applied. The gas burnt quietly with a dimly perceptible flame. In this case, the error in the determination of the hydrogen in the body analysed, consequent upon the use of one of these rolls in the combustion, would have been that due to the occlusion of $\frac{7{\cdot}02}{6} = 1{\cdot}17$ c.c., or 0·00010 grm. hydrogen. That is on the previous assumption that 0·4 grm. substance had been taken for analysis, the error in the percentage of hydrogen would be 0·025 per cent. excess.

*Experiment III.*—Five out of the six rolls of copper-wire gauze used in Experiment II, weighing 79 grms., were subjected to a current of hydrogen at a red heat for 30 minutes and allowed to cool in the same. The amount of hydrogen occluded was then estimated as already described, but this time with the following variation.

Into a portion of the closed end of the tube, which was slightly drawn out, a mixture of bichromate of potash and carbonate of soda was introduced. As soon as the tube had been rendered vacuous, half of the mixture was heated, and the apparatus filled with carbonic acid, which, on issuing at the mercury trough, was tested for air, but found to contain none. The evolution of carbonic acid was then interrupted, and the tube rendered vacuous for the second time. The part of the tube containing the rolls of copper was thereupon heated to bright redness and the pump set working until a third vacuum was obtained, the gas only being turned off from the furnace as the vacuum approached completion. Finally, the apparatus was once more filled with carbonic acid, and the tube rendered vacuous for the fourth time after once more raising the temperature to redness. Both the hydrogen occluded and the carbonic acid last evolved were collected in the

same tube, the latter being absorbed by caustic potash. No absorption on introduction of pyrogallic acid. In this experiment, which, in the main, was a repetition of Experiment I, the 79 grms. copper-wire gauze yielded 1·06 c.c. hydrogen normal.

*Experiment IV.*—This was essentially a repetition of Experiment II, with the variation described under Experiment III. That is to say, perfectly new copper-wire gauze was cut into strips and rolled. Six of these rolls which, after oxidation and reduction, weighed 68 grms., were introduced into a combustion-tube, the somewhat drawn out, closed end of which contained a mixture of bichromate of potash and carbonate of soda. All details of the experiment were the same as just described, and the result was as follows :—

The 68 grms. copper-gauze yield 4·29 c.c. hydrogen normal. No reduction of volume ensued on introduction of pyrogallic acid into the tube.

The conclusions to be drawn from the preceding experiments are the following :—

(1.) That copper-wire gauze which has never been used before, when first oxidised, either in a current of air at a red heat or in the blowpipe flame, and subsequently reduced, and finally allowed to cool in a current of hydrogen, occludes a very appreciable amount of this gas. Experiments II and IV made in this direction, agree well together. Thus, in Experiment II, 96 grms. reduced gauze occluded 7·02 c.c., in Experiment IV, 68 grms. reduced gauze occluded 4·29 c.c. hydrogen, that is, in Experiment II, 0·00065 grm. hydrogen was occluded per 100 grms. of copper, in Experiment IV, 0·00056 grm. hydrogen per 100 grms. of copper. The error consequent upon the use of such gauze in a combustion, on the assumption that 0·4000 grm. of substance be taken for analysis, and that the average weight of a copper roll be 15 grms., is shown to be 0·025 per cent. excess of hydrogen.

(2.) That copper-wire gauze which has been once or several times previously oxidised in air at a red heat, and reduced at a red heat, and allowed to cool in a current of hydrogen, on undergoing these operations again, is found to have lost in great measure its capacity of occluding hydrogen. This may be due, perhaps, to some physical alteration in the metal, as, for instance, in its density. Thus, Experiments I and III, which also agree well together, show that in one case 83 grms. (several times previously reduced) copper gauze occluded 1·07 c.c., in another case, 79 grms. (once previously reduced) copper gauze occluded 1·06 c.c. hydrogen; that is, in Experiment I, 0·000114 grm. hydrogen was occluded per 100 grms. of copper, and in Experiment III, 0·000119 grm. hydrogen per 100 grms. of copper.

The error consequent upon the use of rolls of this gauze in com-

bustions on the previously stated assumptions, is shown to be 0·0039 per cent. excess of hydrogen.

From a consideration of Dumas' observation on the influence of temperature on the occlusive power of copper, and from the effect of red heat aided by the vacuum, it was evident that at a bright red heat copper is incapable of occluding hydrogen, and that the occlusion takes place only on cooling in the current of hydrogen. To test this conclusion, the following experiment was instituted:—

*Experiment V.*—Perfectly new copper-wire gauze was cut into strips and rolled. Six rolls, weighing 57 grms., were, after oxidation in the blowpipe flame, subjected to a current of hydrogen at a bright red heat for some twenty minutes, and while this temperature was maintained, a current of carbonic acid was substituted for that of hydrogen. After maintaining the temperature about twenty minutes longer, the copper was allowed to cool in the current of carbonic acid, and was then transferred to a combustion-tube closed at one end. After drawing out the open end, and placing the tube on the combustion-furnace, this was connected with a Sprengel pump, and rendered vacuous. The temperature was then raised to bright redness, and the pump again set working until, in a few minutes, a second vacuum was obtained. The total amount of gas collected was unmeasurable, being less than 0·1 c.c., and this, on treatment with potash, proved to be carbonic acid.

This result leaves no doubt of the view expressed above, while it indicates a means of entirely obviating any error, however small, which might otherwise be introduced by the use in organic analyses of copper containing occluded hydrogen.

## COMMUNICATIONS FROM THE PATHOLOGICAL LABORATORY OF DR. THUDICHUM.

### IV.—*On Hemine, Hematine, and a Phosphorised Substance contained in Blood-corpuscles.*

By J. L. W. Thudichum and C. T. Kingzett.

#### *On the Composition of Crystallised Hemine.*

The hemine used in the following researches was prepared by one of us by a modification of Wittich's process (*11th Report of the Medical Officer of the Privy Council*, 1869, 155).

This process consists in treating blood with seven times its bulk of a cold solution of potassic carbonate containing one part by weight of

the salt in two parts of water. The thick mixture is filtered on calico, then pressed in cloths, and afterwards treated with alcohol; on standing, the solution which forms containing potassic carbonate is poured off, and the residue, after being freed from liquor by pressing, is now dried at the ordinary temperature. The product is now extracted with warm absolute alcohol at a temperature not exceeding 40° C., and the extracts so obtained are treated with an absolute alcoholic solution of tartaric acid. In this way the potash is precipitated and the hemine remains dissolved, and on evaporation of the solution is precipitated on cooling in very minute bluish-black crystals consisting of rhombic plates. Such a product, after extraction with cold alcohol, ether, and water, and drying in vacuo, constituted the material for the following experiments. On analysis the following numbers were obtained:—

(*a.*) 0·5780 grm. gave 0·0634 grm. $Fe_2O_3$ = 7·677 per cent iron.
" " and 0·0698 " $AgCl$ = 2·98 per cent. chlorine.
" " and 0·0138 " $Mg_2P_2O_7$ = 0·6666 per cent. phosphorus.

(*b.*) 0·514 grm. gave 0·056 grm. $Fe_2O_3$ = 7·625 per cent. iron.
" " and 0·064 " $AgCl$ = 3·08 per cent. chlorine.
" " and 0·0094 " $Mg_2P_2O_7$ = 0·5105 per cent. phosphorus.

(*c.*) 0·5000 grm. gave 0·0607 grm. $AgCl$ = 3·005 per cent. chlorine.
" " and 0·0116 " $Mg_2P_2O_7$ = 0·6479 per cent. phosphorus.

*Synopsis of Analyses.*

| | *a.* | *b.* | *c.* |
|---|---|---|---|
| Iron ..... | 7·677 | 7·625 | — |
| Chlorine ..... | 2·98 | 3·08 | 3·005 |
| Phosphorus ..... | 0·6666 | 0·5105 | 0·6479 |

Hemine has been considered as a hydrochloride of hematine; by others again as a basic hydrochloride or mixture of hydrochloride of hematine, with free hematine. Our researches show that it contains, besides these two bodies, a considerable amount of a crystallisable phosphorised substance. It is thus proved that the crystallised state of substances of such high atomic weight as the body before us is no guarantee of chemical purity or definite composition, an experience which is now also frequently made in the manufacture of artificial dyes.

*Action of dry Hydrochloric Acid gas on Crystallised Hemine.*

·9205 grm. was dried in a current of dry air at 100° in a Liebig's drying apparatus; when dry it weighed ·9034 grm.

Dry hydrochloric acid was now passed over it in the cold and the excess expelled by a current of cold dry air. The gain in weight was 0·0544 grm., or 5·6 per cent. On then heating the bath to 100° C., and continuing the current of air it lost weight; when constant the gain only amounted to 0·0216 grm., or 2·3 per cent.

The tube was now immersed in boiling water and dry hydrochloric acid gas passed through, and after some time dry air was substituted for the hydrochloric acid. The total gain when weight was constant amounted to 0·0310 grm., or 3·3 per cent. This last treatment with hydrochloric acid and subsequently dry air on repetition gave the same figures.

An alcoholic solution of the product was red, but when dilute it was brown in colour. A concentrated solution gave a band in the red, and a slight obscurity near D.

Diluted solution showed a band in red and two bands in green. An ethereal solution of the product gave the three bands most distinctly and unmistakably, but showed all the bands a little moved towards the red end as compared with the alcoholic solution. This experiment shows that crystallised hemine, considered as hematine hydrochloride, is by no means saturated with hydrochloric acid, but contains hematine in the uncombined state; this latter probably takes up some of the hydrodrochloric acid added. But the possibility that the myeline (phosphorised substance) contained also in the hemine may also take up some HCl cannot be lost sight of, and is raised to a probability by the known bearing of myeline from brain-matter.

### *Action of Nitric Acid on Hemine.*

A little crystallised hemine dissolves easily in much nitric acid, imparting a brownish-red colour, perfectly impenetrable to light. The solution takes place without evolution of any gas. From this solution water precipitates red flakes, leaving a nearly colourless fluid containing a little iron in solution.

Preyer, in his little treatise on blood crystals, states that hematine dissolves in nitric acid with decomposition, and that the yellowish solution gives with ammonia (without xanthoproteic reaction) *a white precipitate of hydrated ferrous oxide.* This statement, in itself incredible, because ferrous oxide cannot exist in nitric acid solution, is further contradicted by the above result.

When a nitric acid solution of hemine is so far diluted as to give only a yellowish colour (in which case the hemine present is very minute in amount), ammonia produces no precipitate in it.

When the dark brown nitric acid solution is boiled it evolves some

nitrous fumes, but so slowly as to show that hemine is not readily oxidisable. On addition of water to the solution, a light fawn-coloured precipitate is produced, and the filtrate gives with ammonia *no* precipitate, but only a yellow colour.

Preyer may have mistaken the precipitate produced by the water of his ammonia for protoxide of iron; but this precipitate is soluble in excess of ammonia to a deep yellow colour, and is evidently a decomposition product of hemine.

The precipitate produced as above by water contains nearly the original quantity of iron in combination, so that it remains soluble in strong ammonia, but is destroyed by hydrochloric acid, which, with potassic ferrocyanide, gives the characteristic blue coloration of iron salts.

*Action of Sulphuric Acid on Hemine crystals.*

Some crystals of hemine, after having been extracted with glacial acetic acid, were washed and dried and then treated with oil of vitriol. The purple solution was dissolved in much alcohol and filtered. The red solution gave the spectrum of acid cruentine in alcohol. On rendering the solution alkaline by ammonia, much ammonium sulphate was deposited and separated by filtration. The filtrate gave the spectrum of cruentine in alkaline solution (see *Med. Off. Report*, 1868, 161,) (and 1867, 228).

*Experiments intended to effect the Extraction of Iron from the Hemine.*

We first proceed to notice a paper published by C. Paquelin and L. Jolly (*Compt. rend.*, 79 (1874), 918), entitled "The Colouring Matter of Blood (Hematosine) does not contain Iron." This title, by the implication between brackets, states that the colouring matter of blood is hematosine, or as it is commonly termed in England and Germany hematine. Hematine, however, is only a cleavage-product of the true colouring matter of blood, namely hematocrystalline.

The authors claim to have proved by a previous research (presented to the Academy, March 10, 1873) that the iron present in blood corpuscles exists as tribasic ferrous phosphate, and that the hematosine does not contain iron as an essential constituent. In the paper under consideration they undertake to substantiate this last proposition, and state that they have obtained pure hematosine as follows:—

*First Process.*—Blood is treated with water to dissolve the corpuscles, and the serum-albumin is precipitated by lead acetate. The filtrate is dried and the powdered residue is mixed with five times its weight of

crystallisable acetic acid, with which it is digested during five or six hours at a temperature of 50°. The gelatinous mass thus obtained is now extracted with benzene or carbon disulphide in quantity ten times that of the acetic acid employed. This extraction is repeated during many days, until no more colouring matter is yielded to the solvents. The united extracts are concentrated to a syrup, and then further evaporated to dryness. The residue of amorphous hematosine contains iron and is small in quantity.

*Second Process.*—The globules dried and powdered as above (after treatment with acetic acid) are macerated during eight days with 90 per cent. alcohol containing 10 per cent. ammonia. This extraction is repeated and the united extracts concentrated, when there is left in the retort powdery impure hematosine and water. The hematosine is collected, washed, dried, mixed in a flask with five times its weight of crystallisable acetic acid, and the mixture digested at 50° during some hours, after which the pigment is extracted by means of benzene or carbonic disulphide.

*Purification of Hematosine.*—The authors assume, as the explanation of the above processes, that the acetic acid, by forming acetate of iron with some of the iron, leaves the rest in the form of biphosphate, while the acid also dissolves the albuminous matters. The presence of iron in the ultimate product is explained as due to the solubility of acetic acid in benzene or carbonic disulphide, whereby is dragged into the product ferruginous salt. To remove this iron, the authors tried:

(*a.*) Solvents; such as pure benzene, carbon disulphide, ether, and chloroform, but they all yielded a pigment containing iron.

(*b.*) Caustic soda and potash; but these altered the pigment profoundly, while boiling with dilute ammonia also gave a negative result. All these facts seemed to prove that iron is after all a constituent of hematosine, but they extracted it ultimately from the pigment by the following process:

(*c.*) The pigment was dissolved in ten times its weight of acetic acid, and the liquid mixed with a quantity of citric acid in powder and equal in weight to one quarter of the acetic acid employed. The citric acid was dissolved by gentle heating, more water added, and the whole boiled for one quarter of an hour to aid the solution of the iron. On cooling, the mass became thick from precipitated hematosine, and ammonia was now added to exact neutralisation of the acids, while, if necessary, the whole was allowed to stand for some days to deposit all matters. The hematosine was precipitated as a soft resinous mass, with a pale yellow liquor above it, the latter by ammonium sulphide gave a precipitate of iron sulphide after twenty-four hours. The whole process was repeated upon the hematosine until the final liquors contained no iron. Finally the hematosine was dissolved in ether, and by spontaneous

evaporation gave a black, shining, brittle residue which the authors term *pure hématosine*. It has the following properties:—It burns like resin, leaving no ash, insoluble in water; very little soluble in ammonia, giving a pale yellow coloured solution.

Changed by caustic soda or potash, which reagents assume a brown colour.

Slightly soluble in alcohol, with an amber colour. Soluble in ether, chloroform, benzene, carbon disulphide, with amber colour when dilute, red when concentrated.

The authors promise to furnish the elementary composition of this hématosine in the future.

*Experimental Critique of the above Research.*

In order to test the correctness of the above statements relating to the removal of iron from hematine, by Paquelin and Jolly, we employed a quantity of crystallised hemine, prepared, as already described, by Wittich's process, from ox blood.

*First Experiment.—Action of Acetic and Citric Acids on Hemine.*

1 grm. of hemine was placed in a flask with 10 grms. glacial acetic acid, and 2·5 grms. of citric acid added. The substance did not dissolve in the cold, nor on maintaining the mixture for many hours at 50° did it entirely dissolve. It was now filtered and washed with glacial acetic acid until the filtrates were colourless. In this operation 52 grms. of acetic acid were employed (not including that lost by evaporation). The acid filtrates and matter which remained undissolved were now examined as follows.

(*a.*) *The insoluble portion* weighed, after washing with water and drying, 0·75 grm., and was proved by a special analysis to contain iron, chlorine, and phosphorus. The spectroscopic characters of it in the following solutions were next examined.

1. Alcoholic (87 per cent.) solution acidified with acetic acid. 2. Ammoniacal solution; and the results obtained indicated that the coloured part of the matter under study was ordinary hematine. Like hematine, it proved soluble in concentrated nitric acid, and was precipitated therefrom by water; insoluble in strong hydrochloric acid; little soluble in strong potash.

(*b.*) *The acetic and citric acid solution* gave a spectrum referable to acid hematine. It was neutralised by caustic ammonia, and warmed until the matter was well separated in coloured flakes. These redissolved during 12 hours in much acetic acid, and the solution again gave

an acid hematine spectrum (*Rep. Med. Off.*, 1867, 193 and 224). The conclusion to be drawn, therefore, from this experiment is that the process effects no change in the nature of the hematine.

*Second Experiment.—Hematine, Benzene, and Acetic Acid.*

After the above preliminary experiment was concluded, 8·9 grms. of the same specimen of hemine were placed in a dry vessel with benzene and glacial acetic acid, and shaken therewith during many hours. The extract was drawn off, and the treatment repeated in all three times. The extracts were united, and the undissolved portion was boiled with more benzene and acetic acid during two hours. The extracts, amounting to more than 2 litres, constituted a dark brownish-red solution, which was examined as stated hereafter. The matter undissolved by this treatment was now digested with successive quantities of glacial acetic acid in the hot. The coloured extract of 310 c.c. was proved ultimately to contain only 0·511 grm. substance, which was obtained by neutralisation with ammonia.

The main part of the preparation which remained undissolved in hot acetic acid proved entirely soluble in dilute ammonia.

*The ammoniacal extract* on being rendered neutral by acetic acid deposited the whole of its hematine, which was isolated and washed with large volumes of water, then dried, and analysed. It weighed 5·4 grms. It was of a black glistening appearance. Dried at 100° C.

(*a.*) 0·5470 grm. gave 0·0710 grm. $Fe_2O_3$ = 12·979 per cent. $Fe_2O_3$ or 9·085 per cent. iron. (Lecanu found in a specimen of ox hematine 12·76 per cent. $Fe_2O_3$, or 9·018 per cent. Fe.) *The preparation was free from chlorine and phosphorus.*

(*b.*) 0·0242 grm. gave by combustion *in vacuo* 28·1 c.c. of normal carbonic acid, and 1·7 c.c. of nitrogen, normal, or 62·25 per cent. carbon, and 8·78 per cent. nitrogen. Here the relation of N to C is as 1 : 8·2.

(*c.*) 0·3653 grm. gave 0·828 grm. $CO_2$ and 0·1698 grm. $H_2O$ = 61·81 per cent. carbon and 5·16 per cent. hydrogen.

| | | | | | |
|---|---|---|---|---|---|
| C .... | 61·81 | + by atomic weights = | 5·151 | + by Fe = 1 | 31·8 |
| H .... | 5·16 | | 5·16 | | 31·8 |
| Fe.... | 9·08 | | ·162 | | 1·0 |
| N .... | 8·78 | | ·627 | | 3·8 |
| O .... | 15·17 | | ·948 | | 5·8 |

or $C_{32}H_{32}FeN_4O_6$.

This preparation, therefore, was hematine, in which the iron had not only not been diminished by the process of Paquelin and Jolly, but

which contained more iron than has ever before been found in any preparation of hematine.

We have no intention here to exhaust the question of the composition of pure hematine, but in passing we may refer to the statements of Hoppe-Seyler concerning its composition. This author, abandoning several previous varieties of formulæ, now gives $C_{34}H_{34}N_4FeO_5$ as that of pure hematine. But on inspection of his analytical results, it is seen that he finds an excess of nitrogen, which he explains by the assumption that the hematine while being washed on the filter absorbed ammonia from the air, which it retained obstinately on drying. Our experience controverts this assumption, as it shows that mere vestiges of ammonia which the water may absorb from the air will immediately dissolve the hematine and cause it to pass through the filter. This solubility is in fact so striking as to constitute a delicate test for such small amounts of ammonia as can otherwise be revealed only by the Nessler test. This observation was once made when the hematine was being washed with water which had been specially rendered free from ammonia. Suddenly the washings came through coloured, and on testing the water by the Nessler test it was found to have absorbed from the laboratory atmosphere traces of ammonia. From such coloured washings any hematine is entirely reprecipitated in flocks by a drop of acetic acid.

*Isolation of the Phosphorised Body.*

*The benzene and acetic acid extracts* were freed from benzene by distillation, and left a black viscous mass which proved for the most part soluble in hot absolute alcohol. It left, however, insoluble 0·5 grm. of a chocolate coloured powder.

The alcoholic solution had a red colour, and showed a diffuse acid hemine spectrum. After most of the alcohol had been removed by distillation, *a colourless matter* was deposited, which on being again dissolved in alcohol gave precipitates with $PtCl_4$, $CdCl_2$, and $Pb(C_2H_3O_2)_2$.

The whole solution was now precipitated with alcoholic cadmic chloride, and the colourless precipitate washed. It had the following characters :—

Soluble in hot alcohol; reprecipitated on cooling On burning gives out a fatty smell; fuses, and leaves a charcoal with much phosphoric acid.

Finally the whole of the $CdCl_2$ precipitate was recrystallised from alcohol and analysed.

The alcoholic mother-liquors retained all the hematine present originally with the phosphorised body.

*Analyses of Substance dry at* 100° C.

(*a.*) 0·2543 grm. gave 0·0413 grm. CdO = to 14·07 per cent. cadmium, and 0·0934 grm. AgCl = to 9·08 per cent. chlorine, and 0·31 grm. $Mg_2P_2O_7$ = to 3·404 per cent. phosphorus.

(*b.*) 0·290 grm. gave 0·5304 grm. $CO_2$ = 49·88 per cent. C., and 0·234 grm. $H_2O$ = 8·96 per cent. H.

(*c.*) 0·0246 grm. gave by combustion *in vacuo* 25·9 c.c. normal $CO_2$, and 0·5 c.c. N, normal, showing relation of N : C to be 1 : 26.

Thus we have the following figures:—

| | Per cents. | ÷ at. wgts. | ÷ P = 1. |
|---|---|---|---|
| C ..... | 49·88 | 4·156 | 38·1 |
| H ..... | 8·96 | 8·96 | 82·2 |
| N ..... | 2·54 | ·181 | 1·6 |
| P ..... | 3·404 | ·109 | 1·0 |
| O ..... | 12·066 | ·754 | 6·9 |
| Cd ..... | 14·07 | ·125 | 1·1 |
| Cl ..... | 9·08 | ·255 | 2·3 |

These figures therefore give a formula of $C_{76}H_{164}N_3P_2O_{14}(CdCl_2)_2$. Now deducting the $CdCl_2$, and recalculating the per cents. of the other elements, we obtain figures which when compared with figures obtained in the same way, and relating to a cadmic chloride salt (also recrystallised from alcohol) of one of the forms of myeline from brain matter, show remarkable evidences of identity of these principles (see *Rep. Med. Off.*, new series, No. iii [1874], 174).

| | Phosphorised principle from blood-corpuscles. | Phosphorised principle from brain. |
|---|---|---|
| C..... | 64·90 | 64·66 |
| H ..... | 11·65 | 11·30 |
| N ..... | 3·30 | 3·11 |
| P..... | 4·42 | 4·15 |
| O..... | 15·72 | 16·78 |

The presence of phosphorised principles in the blood has been repeatedly observed, but the isolation and analysis of any definite substance has for the first time been effected in this research. We do not say that this is the only phosphorised substance present in blood corpuscles, as, for example, the bodies of the kephalin series might also be represented in the blood, but would have been excluded from the hemine by our mode of preparation.

The further conclusions to be drawn from these researches are that the statements of Paquelin and Jolly relative to the extraction of the iron from hematine are entirely incorrect, while it is apparent that

they succeeded in extracting by their process a coloured impurity of hematine, which they name hematosine. The nature of this coloured substance cannot be criticised any further, as they fail to give any elementary analyses.

The circumstance that they found the iron of their hematosine combined with phosphoric acid also reveals that their preparation was contaminated with the phosphorised myeline. The ferric ash of pure hematocrystalline and pure hematine contains no phosphoric acid.

# ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

## General and Physical Chemistry.

### New Observations on the Susceptibility to Light of Silver Bromide. By H. W. Vogel (Deut. Chem. Ges. Ber., ix, 667—670).

Some bodies, such as pyrogallic acid, gallic acid, and morphine, which render iodide of silver more sensitive to the action of light, produce the reverse effect on the bromide of silver. It has also been shown that iodide of silver differs in its behaviour according as it has been formed with excess of silver nitrate or of iodine. According to Schulz-Sellack, the iodide prepared with excess of iodine is twenty times less sensitive than that prepared with excess of silver nitrate. Bromide of silver exhibits a similar behaviour in a lesser degree. The senitiveness of bromide of silver precipitated with excess of bromine is, however, considerably increased by the presence of such bodies as tannin, morphine, yellow prussiate of potash, &c. The reason is that a trace of silver nitrate is left when excess of this body has been employed, and this acts far more energetically than organic bodies in promoting sensitiveness; the addition of tannin, &c., causes the decomposition of this trace of nitrate and hence lowers the sensitiveness of the plate; but when excess of bromine is present during the formation of the bromide of silver no nitrate is mixed with it, and so the addition of tannin, &c., promotes sensitiveness.

Many colouring matters *e.g.*, cyanin, eosin, naphthalene red, render a bromide of silver plate more susceptible under certain circumstances to the yellow and red than to the blue rays. Tannin and morphine also promote sensitiveness to yellow rays when they are dissolved in naphthalene red and painted over the plate. The author draws a distinction between those bodies which act from their capability of optical absorption, and bodies, such as tannin, which chemically combine with iodine and bromine. The statement (*Berichte*, viii, 1635) that the disadvantage caused by too strong coloration of the layer of silver bromide could be avoided by illumination on the back of the plate is contradicted.

G. T. A.

### Influence of Temperature on the Circular Polarisation of Quartz. By V. von Lang (Pogg. Ann., clvi, 422—429).

This paper records investigations which prove that the angle of rotation for quartz changes with the temperature. The change is relatively the same for rays of all colours, and the value of the angle for a given temperature, $t^\circ$, is $\delta_0$ $(1 + \cdot 000149\ t)$, where $\delta_0$ is the angle at 0° C.

R. R.

**Experiments with Crookes' Radiometer.** By R. BÖTTGER (Deut. Chem. Ges. Ber., ix, 798—800).

AN instrument constructed by Dr. Geissler in Bonn did not move on exposure to the light of the full moon, or of a Geissler's tube made phosphorescent by magnesium light. On placing between it and a bright gas flame distant 24 centimeters a clear alum plate of 5 mm. thickness, the vanes moved very slowly, the plate being not perfectly athermanous; while a layer of water of 9 mm. thickness prevents the motion completely. This shows that the instrument is affected only by radiant heat.

When the radiometer is exposed in a room of the temperature of 15° to a bright flame, the vanes move with the white sides in front, but putting it now in water of 45°, the motion first ceases and then is reversed, *i.e.*, the black sides being now in front.

Another instrument, made by Mollenkopt in Stuttgart, moved in gas-light like Geissler's, but when it was placed in hot water, no change in the direction of the rotation took place, nor did it slacken if some ether was poured on the globe while the vanes were put in motion by gas-light, whereas in the Bonn instrument under this condition the motion became much slower.

C. S.

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**A Lecture-experiment on the Spectrum.** By F. KESSLER (Deut. Chem. Ges. Ber., ix, 577—578).

To obtain the solar spectrum the rays, after having passed through several prisms, are usually thrown on the screen by a lens. If, instead of the latter, a concave mirror is employed in such way that the rays, after passing the prisms, are sent back through them, only half the number of them may be employed, or with a given number the double effect is obtained. The arrangement is explained by diagrams.

C. S.

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**Alleged replacement of Electro-positive by Electro-negative Metals in a Voltaic Cell.** By W. SKEY (Chem. News, xxxii, 213).

OBJECTION is taken to the experiments on which Gladstone and Tribe base their argument for the replacement of electro-positive by electro-negative elements. These observers found that when zinc and platinum are connected voltaically in a solution of chloride of potassium, "potassium is set free, manifesting itself by the presence of free alkali and hydrogen." The alkalinity of the liquid is not, however, according to the author, proof of the liberation of potassium. Thus an aqueous solution of potassium chloride with zinc becomes alkaline, so also does the same liquid with pure silver. In the first case we have probably decomposition of water and formation of ammonia, aided perhaps by formation of zinc oxide, with subsequent production of zinc oxychloride. In the latter case we have oxidation of silver by free oxygen present, and subsequent reaction of the oxide to form caustic potash and silver chloride. To another experiment, viz., the decomposition

of mercuric chloride with production of mercurous chloride and mercury by means of mercury and gold in conjunction, objection is taken on the ground that, if the experiment be carried out in absence of light and dust only a trace of the lower chloride is obtained, but no mercury.

M. M. P. M.

## Dielectric Constants of Liquids.

By P. SILOW (Pogg. Ann., clvi, 389—396).

FOR the determination of these constants the author constructed a modification of Thomson's quadrant electrometer, so arranged that the needle could be readily surrounded with any liquid dielectric. A constant potential was maintained by connection with the pole of a galvanic arrangement formed with copper, zinc, and distilled water.

R. R.

## Voltaic Polarisation of Aluminium.

By W. BEETZ (Pogg. Ann., clvi, 456—465).

THE paper describes the apparatus and experiments by which the author measured the polarisation of aluminium electrodes. The results agree well with those which Tait obtained by another method.

R. R.

## Easily prepared Galvanic Cells. By ONIMUS (Compt. rend., lxxxii, 1192—1193).

THE improvement consists in using vegetable parchment to wrap round the zinc, and securing it in its place by a copper wire which serves instead of a copper plate. If a carbon battery be preferred, the cylinder of carbon is surrounded by vegetable parchment, and the latter secured in its place by thick zinc wire, or by a piece of sheet zinc.

W. R.

## Welter's Law and the Latent Heat of Carbon-vapour.

By G. BETHKE and F. LÜRMANN (Dingl. polyt. J., ccxx, 182—184).

WELTER'S law, that "equal weights of oxygen on combustion with any substance develop equal quantities of heat," was founded on the researches of Despretz, Lavoisier, and Clement, who assigned to hydrogen the number 24,000 heat-units in burning to water, and 8,000 to carbon in burning to carbon dioxide.

1 part by weight of carbon requires $2\frac{2}{3}$ parts of oxygen in burning to carbon dioxide.

1 part by weight of hydrogen requires 8 parts of oxygen in burning to water.

Then 1 part of oxygen develops in combustion with carbon $\frac{8000}{2\frac{2}{3}} = 3{,}000$ heat-units; and

1 part of oxygen develops in combustion with hydrogen $\frac{24000}{8}$ = 3,000 heat-units.

Thus Welter founded his law.

The authors show that although more recent researches by Dulong, Favre and Silbermann, and Grassi have altered the number for hydrogen from 24,000 to 34,000 approximately, thus causing that for 1 part of oxygen as above to become $\frac{34000}{8}$ = 4,250, instead of 3,000, yet the truth of Welter's law does not suffer in the least, but, on the contrary, is confirmed.

1 part of hydrogen burnt to water develops, according to the more recent investigations, 33,600 heat-units.

1 part of carbon monoxide burnt to carbon dioxide develops, according to the more recent investigations, 2,400 heat-units.

1 part of carbon burnt to carbon monoxide develops, according to the more recent investigations, 2,400 heat-units.

1 part of carbon burnt to carbon dioxide develops, according to the more recent investigations, 8,000 heat-units.

Then 1 part of oxygen develops in combustion with hydrogen $\frac{33680}{8}$ = 4,200 heat-units.

1 part of oxygen in burning carbon monoxide to carbon dioxide develops $\frac{2400}{\frac{4}{7}}$ = 4,200 heat-units.

On the contrary,—

1 part of oxygen in the combustion of carbon to carbon monoxide develops $\frac{2400}{\frac{4}{3}}$ = 1,800 heat-units; and

1 part of oxygen in the combustion of carbon to carbon dioxide develops $\frac{8000}{\frac{8}{3}}$ = 3,000 heat-units.

The above apparent discrepancy is due to heat which has become latent in the vaporisation of the solid carbon, and is required to maintain it in the gaseous form. This apparent error appears always, therefore, on the combustion of solid carbon to gaseous carbon monoxide or dioxide, but of course does not appear in the oxidation of carbon monoxide to carbon dioxide, both being gaseous bodies.

The following deductions may now be made:—

In the combustion of carbon monoxide to carbon dioxide $\frac{4}{7}$ part of oxygen unites with $\frac{3}{7}$ part of gaseous carbon, developing 2,400 heat-units.

For 1 part of gaseous carbon, then, are developed $\frac{2400}{\frac{3}{7}}$ = 5,600 heat-units.

By direct experiment, 1 part of solid carbon burning to carbon monoxide gives 2,400 heat-units.

The difference is the heat becoming latent in effecting the change from solid to gas, 3,200 heat-units.

1 part of solid carbon burning to carbon monoxide develops

$$\left.\begin{array}{ll}\text{latent} & .. \ 3{,}200 \\ \text{sensible} & .. \ 2{,}400\end{array}\right\} = 5{,}600 \text{ heat-units.}$$

1 part of solid carbon burning to carbon dioxide gives $5{,}600 \times 2 =$

$$\left.\begin{array}{ll}\text{latent} & .. \ 3{,}200 \\ \text{sensible} & .. \ 2{,}400 \\ \text{sensible} & .. \ 5{,}600\end{array}\right\} 11{,}200 \text{ heat-units.}$$

It may be observed that,—

1 part of oxygen in the combustion of carbon to carbon monoxide develops totally $\frac{5600}{\frac{4}{3}} = 4{,}203$ heat-units.

1 part of oxygen in the combustion of carbon monoxide to carbon dioxide develops a total of $\frac{11200}{\frac{8}{3}} = 4{,}200$ heat-units.

Another form may also be given to Welter's law, as below:—

"Every simple and compound body by combustion with oxygen develops the following quantity of heat:—33,600 heat-units (the heat of combustion of hydrogen to water) divided by the atomic weight of the body, and multiplied by the number of atoms of oxygen required."

$$O = 8 \qquad H + O = \frac{33600}{1} = 33{,}600.$$

$$C = 6 \qquad C + O = \frac{33600}{6} = 5{,}600.$$

$$C + 2O = 2\frac{33600}{6} = 11{,}200.$$

$$CO + O = \frac{33600}{14} = 2{,}400.$$

W. S.

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## On Dissociation.

By A. Horstmann (Deut. Chem. Ges. Ber., ix, 749—758).

The author has repeated Isambert's experiments on the dissociation of the compounds of ammonia with silver chloride. The apparatus employed consisted of a glass flask containing dried silver chloride placed in the middle of a large vessel of water of known temperature, and connected with a Sprengel mercurial pump and manometer. Pure and dry ammonia was admitted to the flask from a second flask containing a larger quantity of silver chloride and ammonia, from which the ammonia could be expelled by heat. In the construction of the apparatus caoutchouc tubing was entirely avoided. The results fully confirmed the conclusions previously arrived at by Debray and Isambert. The tension of the ammonia was found to be dependent on temperature only, not on the degree of saturation or decomposition of the compound. On admitting ammonia to silver chloride partially saturated with ammonia, the pressure thereby increased gradually sank, owing to absorption of the gas; and conversely, on pumping out ammonia, the pressure thereby lowered gradually rose; and whether sinking or rising the pressure approximated to the same point, show-

ing clearly the existence of an equilibrium, which could be determined within the limits of errors of observation, by making the differences of pressure small enough. For details of the method of working, the original paper must be consulted. The results arrived at with the compounds ($AgCl.3NH_3$) and ($2AgCl.3NH_3$) are given in the following table :—

| Temp. C. | Tension in millimeters. | | | |
|---|---|---|---|---|
| | $AgCl.3NH_3$. | | $2AgCl.3NH_3$. | |
| 6 | | | 22·0 | Diff. |
| 7 | | | 23·4 | 1·4 |
| 8 | 432 | Diff. | 24·9 | 1·5 |
| 9 | 446 | 14 | 26·5 | 1·6 |
| 10 | 465 | 19 | 28·2 | 1·7 |
| 11 | 491 | 26 | 30·0 | 1·8 |
| 12 | 520 | 29 | 31·9 | 1·9 |
| 13 | 551 | 31 | 33·9 | 2·0 |
| 14 | 584 | 33 | 36·0 | 2·1 |
| 15 | 618 | 34 | 38·3 | 2·3 |
| 16 | 653 | 35 | 40·9 | 2·6 |
| 17 | 688 | 35 | 43·7 | 2·8 |
| 18 | 723 | 35 | 46·6 | 2·9 |
| 19 | 758 | 35 | 49·6 | 3·0 |
| 20 | 793 | 35 | 52·6 | 3·0 |
| 21 | 829 | 36 | 55·6 | 3·0 |

J. R.

## Quantivalence.

By J. Janovsky (Deut. Chem. Ges. Ber., ix, 696—701).

In reply to Horstmann, the author says that the quantivalence of an element is a function of its atomic and equivalent weights. As the former is constant, the quantivalence can change only if the equivalent is variable. The latter is the case if we mean by quantivalence the number of monad atoms which can combine with an element, but if quantivalence means the highest number of monads, then the quantivalence is constant.

Each element has only one equivalent, if we mean by this term the quantities of an element which unite with the unit of weight of another element, with the same expenditure of work. If one and the same galvanic current precipitates from cuprous chloride twice as much copper as from cupric chloride, it shows that the work done is not the same; in the first case the excess of work is changed into heat, just as heat is evolved when cuprous chloride combines with chlorine to form cupric chloride.

If we say that iron is a tetrad in ferrous chloride, and a hexad in ferric chloride, we regard both as saturated compounds, which is not correct, because the former combines directly with chlorine; and if we consider ethene as a saturated compound, we must assume that when it combines with hypochlorous acid it first becomes non-saturated in

order to get saturated again. The definition of a saturated compound would then be a body which either does not combine with other atoms, or combines with one or more atoms. That many non-saturated compounds behave like saturated bodies, and that some of the former are more stable than some of the latter, only shows that the attraction of the more distant atoms in the molecule is weaker than those which are closer together.

In conclusion the author gives a mathematical deduction of the equation EQ = JH, which he has used in his former paper.

C. S.

**Condensation of Vapour of Mercury on Selenium in the Sprengel Vacuum.** By R. J. Moss (Chem. News, xxxii, 203).

A BAR of selenium placed in the Sprengel vacuum acquired a high degree of conductivity after some days. A bar of selenium immersed in mercury for six weeks likewise became coated with a highly conducting film. In an experiment conducted with the object of observing how much mercury was needed to cause the conductivity, no sensible decrease in the globule of mercury, enclosed with the selenium in an exhausted tube, could be noticed. The formation of the conducting film may be stopped by the admission of air: hence it is easy to prepare bars of selenium of any given high resistance with accuracy.

M. M. P. M.

**Note on certain Hydrates.** By A. H. CHURCH (Chem. News, xxxii, 203).

To express the loss of combined water from insoluble transparent crystals, where no change in the smoothness of the surface occurs, but the crystal becomes more or less opaque, the author proposes the name *nebulescence*. He proposes to divide hydrates into three classes, according as they retain their combined water because of lowness of temperature, moistness of air, or medium or high barometric pressure. The first class he calls, in accordance with Guthrie, *cryohydrates*, the second *hygrohydrates*, and the third *barohydrates*.

M. M. P. M.

**New Experiments on the Flexibility of Ice.** By J. J. BIANCONI (Compt. rend., lxxxii, 1193, 1194).

ICE, at a temperature of 1° to 5° R, was slowly moulded by a granite block placed on its surface. Ice may also be bent, if the pressure is applied for a sufficiently long time.

W. R.

# Inorganic Chemistry.

**Determination of the Atomic Weights of Caesium and Rubidium.** By F. GODEFFROY (Liebig's Annalen, clxxxi, 176—191).

THE author, after having tried the different methods for separating caesium, rubidium, and potassium, prefers Redtenbacher's, which consists in preparing the alums and separating these by fractional crystallisation. 100 parts of water dissolve at 17° of:

| Potassium-alum. | Rubidium-alum. | Caesium-alum. |
|---|---|---|
| 13·5 | 2·27 | 0·619 |

By a continued methodical fractionation he obtained the following crystallisations:—

Pure caesium-alum.
The same, ditto, containing traces of rubidium.
Rubidium-alum with traces of caesium.
Pure rubidium-alum.
The same, ditto, with traces of potassium.
Potassium-alum with traces of rubidium.

The pure alums were converted into the pure chlorides by precipitating their hot solution with pure ammonia, evaporating the filtrate in a platinum-basin, igniting the residue, dissolving the fused mass in water, and adding pure barium chloride as long as a precipitate was formed. After filtering, pure ammonia and ammonium carbonate were added to the warm solution, and after standing for some time, the solution was again filtered, evaporated, and fused. This process was repeated, and then the chlorides crystallised. The pure caesium chloride thus obtained was not in the least deliquescent, and the determination of chlorine gave, as mean of four very nearly agreeing results, the atomic weight of caesium = 132·557, if Cl = 35·46 and Ag = 107·94, while that of rubidium was found = 85·476 as mean of four experiments.

To remove rubidium from caesium-alum containing traces of it, the author used a method which he has already described. The salt was converted into the chloride, which was dissolved in strong hydrochloric acid and precipitated by an acid solution of antimony chloride. The precipitate, after being washed with hydrochloric acid, is free from rubidium. On treating it with water, antimony oxychloride separates out: if the solution is evaporated and ignited with sal-ammoniac, all the remaining antimony volatilises and pure caesium chloride is left behind.

On treating rubidium-alum containing caesium in a similar way, the precipitate obtained contains traces of rubidium, which may be removed by dissolving in dilute hydrochloric acid and precipitating again by the concentrated acid. Other chlorides of the heavy metals also give precipitates with caesium chloride in presence of strong hydrochloric acid, and the sulphate is precipitated by the sulphates of these metals

when dissolved in dilute sulphuric acid; potassium- and rubidium-salts do not give this reaction. The picrates of rubidium and caesium resemble potassium picrate, being sparingly soluble in water, and very sparingly in alcohol.

C. S.

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**Etched Figures on Cubes of Rock-salt, and some Remarks upon F. Exner's Method for the Production of Figures by Solution.** By L. SCHNECKE (Pogg. Ann., clvii, 329—335).

LEYDOLT was the first to point out that different figures could be obtained by the action of certain solvents upon crystals, and that this fact was of great importance in determining the structure of crystals. (*Sitzungsber. d. Wiener Akad.*, 1855, Bd. 15, 59—81.) He described the action of damp air upon a crystal of rock-salt as resulting in four-faced depressions, formed out of the faces of the same tetrakis-hexahedron $\infty O2$ into which a rock-salt crystal is gradually developed (according to Mohs) by the action of moist air. Exner obtained, on the contrary, square depressions by the action of a stream of water dropping perpendicularly upon the crystal face. The author modified the latter method by suspending a crystal of rock-salt in a concentrated solution of the same, when after the lapse of some time depressions were observed, which were formed out of four pyramidal faces, the bottom of the depression being a square whose edges were parallel with the upper edges of the depression, but also slightly distorted. On allowing the crystal to remain in the solution for some days, the edges lost their distinctness and the cube eventually changed into a round indeterminable tetrakis-hexahedron. It will be apparent from the above that Exner's method is not adapted to the formation of symmetrical figures possessing distinct, well defined edges, owing to the too rapid action of the solvent. This fact becomes more apparent on comparing the results obtained by Exner on alum crystals by the action of solvents, with those obtained by Leydolt from the same substance. The latter observed that the action of water on alum crystals produced three-sided pyramidal depressions on the octohedral faces, their outline being an equilateral triangle having an inverse position to the face of the octohedron, whilst at the bottom of each of the depressions there is a small equilateral triangle whose sides are parallel with the upper edges. On substituting Exner's method different results are obtained. The edges of the depressions produced resemble an equilateral triangle with truncated angles, or a "hexagon;" they were not well defined but much rounded. The author considers these "hexagons" to be equilateral triangles which could not properly develop themselves owing to the too violent action of the solvent. Leydolt did not give any measurements to prove his assertion that the depressions on rock-salt were formed by faces of $\infty O2$. Schnecke made a series of measurements in order to determine crystallographically the proper formulæ of the forms. These measurements were very uncertain, as the depressions could scarcely be detected by the naked eye, and had to be examined under the microscope; they were also rounded and often rough, making it still more difficult to obtain

good results. G. Rose's method was adopted by the author, and a very narrow bundle of rays was allowed to fall upon the crystal in order to ensure their having a certain direction. The crystal depressions submitted to measurement had been variously obtained, viz., (1) by the action of moist air; (2) through the action of a stream of concentrated salt solution; (3) and (4) through suspension in concentrated salt-solutions for 6 and 15 hours respectively. The normal angle, *w*, is that of two adjacent faces, and the measurements were repeated very often and the mean taken, as follows:—

| *Etched figures of uncertain origin.* | | | *Etched figures obtained by the action of solvents.* | |
|---|---|---|---|---|
| | Pyramid. | Angle *w*. | Pyramid. | Angle *w*. |
| No. 1. | 1st pair of faces | 7° 34′ | 1 | 7° 18′ |
| No. 1. | 2nd ,, | 7° 46′ | 2 | 7° 22′ |
| No. 2. | | 8° 40′ | 3 | 8° 15′ |

* The last given measurement refers to the angle between two faces lying opposite to each other, and the angle *w* is calculated from it.

*Etched figures obtained by suspension for six hours in a solution of Salt.*

| | Pyramid. | Angle *w*. |
|---|---|---|
| No. 1. | 1st pair of faces | 7° 25′ |
| No. 1. | 2nd ,, | 8° 50′ |
| No. 2. | | 8° 32′ |
| No. 3. | | 8° 54′ |
| No. 4. | | 9° 12′ |
| No. 5. | | 11° 1′ (?) |

*Etched figures obtained by suspension for fifteen hours in a solution of Salt.*

| | Pyramid. | Angle *w*. |
|---|---|---|
| 1. | | 8° 49′ |
| 2. | | 3° 1′ |
| 3. | | 10° 37′ |
| 4. | | 12° 38′ |
| 5. | | 14° 14′ |

The values for the co-efficient *n* in the formula $a : na : \infty a$ (corresponding to the values of the angle *w*), are as follows:—

| *w*. | 7°. | 8°. | 8° 4⅕′. | 8° 57¼′. | 9°. | 14°. |
|---|---|---|---|---|---|---|
| n | 11·55 | 10·09 | 10 | 9 | 8·96 | 5·72 |

Thus it is readily seen that the observed etched figures are formed by various obtuse tetrakis-hexahedrons, varying from $\infty O5{\cdot}7 : \infty O11{\cdot}5$; the commonest being $\infty O9$ and $\infty O10$, whilst that observed by Leydolt, viz., $\infty O2$, does not occur. The author considers it probable that none of the etched figures obtained on rock-salt can be referred to a definite tetrakis-hexahedron.

C. A. B.

## On a New Sulphate of Potassium.

By J. OGIER (Compt. rend., lxxxii, 1055—1057).

POTASSIUM sulphate crystallises from a solution containing excess of potassium benzenesulphonate in large, thin laminæ, containing $\frac{1}{2}$ a molecule of water. It contains a trace of the latter salt. Sulphate of copper crystallises with 36 per cent. of water when the analogous copper salt is present.

W. R.

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## Extraction of Gallium from its Ores.

By LECOQ DE BOISBAUDRAN (Compt. rend., lxxxii, 1098—1100).

THE blende is dissolved in aqua regia, and slips of zinc are immersed in the solution and withdrawn when the evolution of hydrogen has almost but not entirely ceased; by this means the Cu, Pb, Cd, Ir, Tl, Ag, Hg, Se, As, &c., are for the most part removed. A great excess of zinc is added to the clear fluid, which is then boiled for some hours; an abundant gelatinous precipitate then comes down consisting of alumina, basic salts of zinc, and gallium. This precipitate is redissolved in hydrochloric acid; ammonium acetate is added, and the alumina precipitated with sulphuretted hydrogen. The solution in hydrochloric acid of the white sulphides is fractionally precipitated with sodium carbonate; the gallium is found in the first portions; the point where the precipitation may be stopped is easily recognised by spectroscopic examination. The gallium is separated from the zinc by solution in sulphuric acid and addition of excess of ammonia. Much of the gallium remains dissolved in the ammonia which is recovered by boiling till excess of ammonia is expelled; the excess of ammonia salts is then decomposed with aqua regia; and the gallium and zinc are separated by fractional precipitation with sodium carbonate. The pure gallium oxide precipitated by ammonia is dissolved in potash and electrolysed; the gallium is deposited on the negative electrode. Five or six Bunsen's cells are able to decompose 20 or 30 cubic centimeters of a strong solution. The gallium is easily separated from the platinum by bending it under cold water.

The author found gallium in considerable quantity in black blende from Bensberg, yellow blende from Asturias, and brown blende from Pierrefitte (Pyrenees).

W. R.

## Zirconium-compounds.

By RICHARD HORNBERGER (Liebig's Annalen., clxxxi, 232—241).

THE following process is recommended for preparing pure zirconium chloride:—Zircon or hyacinth heated to redness and slaked in water is coarsely powdered and fused with 3 or 4 parts of potassium bifluoride, $KHFl_2$, in a platinum crucible. The fused mass is powdered and boiled with water containing hydrofluoric acid, which on cooling deposits fine rhombic crystals of potassium and zirconium fluoride. This double salt is decomposed by sulphuric acid, the solution is pre-

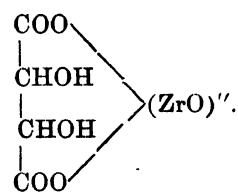
cipitated with ammonia in the cold, and the zirconium hydrate thus obtained is washed with cold water and ignited. The oxide is finally converted into chloride by igniting it with charcoal in a current of chlorine.

The author has endeavoured in vain to obtain organic compounds of zirconium analogous to the ethers of silicic acid.

When zirconium sulphate is mixed with an equivalent quantity of barium sulphocyanate, barium sulphate is precipitated, whilst zirconium sulphocyanate remains in solution. The latter solution decomposes rapidly, depositing a yellow powder, and afterwards contains a substance agreeing in composition with the formula $Zr(CNS)_2$.

Potassium ferrocyanide added to a solution of a neutral salt of zirconium produces a yellowish-white precipitate insoluble in excess, and giving on analysis numbers agreeing with the formula $Fe_2Zr_3(CN)_{12}$, which is analogous to that of Turnbull's blue, $Fe_2Fe_3(CN)_{12}$.

Tartrates of the alkalis produce in solutions of zirconium a white precipitate of zirconium tartrate, which is soluble in potash, in excess of tartaric acid, and in neutral sodium tartrate. The probable constitution of this body, as deduced from analysis, is thus represented:—




The mother-liquor of this salt contains other compounds richer in zirconium, the constitution of which is not yet made out.

J. R.

## Metallic Cerium, Lanthanum, and Didymium.

By Hillebrand and Norton (Pogg. Ann., clvi, 466—476).

The paper describes at length the processes by which the compounds of the respective metals were separated from each other, their reduction by electrolysis, and the subsequent treatment of the products, by which the metals were finally obtained pure and in the massive state. The following are some of the characters which the metals are described as presenting:—

*Cerium* has the colour and lustre of iron, and takes a high polish; in dry air it preserves its lustre, but in moist air it becomes covered with coloured films like heated steel. It is malleable, and when hot can be drawn into wire of remarkable flexibility. Its melting point is below that of silver; but considerably above that of antimony. It kindles in the air at a lower temperature than is required to ignite magnesium; small fragments inflame by the mere act of detaching them, and showers of brilliant sparks are produced by striking a piece of the metal with a flint. A piece of cerium wire burns with even greater brilliancy than magnesium. Cerium burns in chlorine and in

bromine vapour, and combines directly with iodine, sulphur, and phosphorus. Concentrated sulphuric and nitric acids do not attack it in the cold, but when diluted these acids dissolve it readily, as does also hydrochloric acid.

*Lanthanum*, in its general chemical behaviour, resembles cerium; it is, however, readily attacked by strong nitric acid, and it quickly becomes covered with a steel-blue film even in dry air. Though malleable, it is not ductile. It requires for ignition a much higher temperature than cerium.

*Didymium* ranks more closely with lanthanum than with cerium in its chemical relations, but the resemblance to the former element does not extend to the physical properties. It is moreover altered even by dry air, and in presence of moisture receives a yellow film. The absorption-bands which characterise the salts of didymium are not produced by the light which is reflected from a polished surface of the metal.

The specific gravities of various samples of the three metals all range between 6·0 and 6·7. Between 0° and 200° the thermo-electric series runs;—iron, lanthanum, cerium, didymium, magnesium; and the order of the electromotive forces when water is the exciting fluid, is, zinc, cerium, lanthanum, didymium, magnesium.

R. R.

## The Nitrides and Carbides of Niobium and Tantalum.

By A. Joly (Compt. rend., lxxxii, 1195—1197).

By heating to the temperature of melting iron, in a carbon crucible a mixture of niobic acid, sodium carbonate, and pure carbon, or, even a niobate containing little alkali, an olive-coloured crystalline residue was obtained. On continuing the heat for a longer or shorter time, this residue was found to have the formula—

$$NbC + \tfrac{4}{5}NbN, \text{ and } NbC + \tfrac{2}{3}NbN.$$

At the temperature of melted nickel, when the heat was kept up for 6 or 7 hours, long greyish-violet needles were formed, of the formula, $NbC.\frac{1}{5}NbN$. When they are treated with chlorine no oxychloride of niobium is formed, showing that all oxygen had been expelled. These substances when heated in air give a bulky residue of niobic anhydride. Tantalic acid, treated in the same way gave a substance of the formula $TaC + \frac{1}{10}TaN$. When ammonia gas is passed over tantalum chloride, at a temperature rather higher than is sufficient to volatilise the ammonium chloride formed, an ochre-red mass remains, which has the formula, $Ta_3N_5$. The equation is—

$$3TaCl_5 + 5NH_3 = Ta_3N_5 + 15HCl.$$

When this substance is heated to whiteness in perfectly dry ammonia gas, a black substance is formed, of the formula TaN, and this substance is partially transformed into carbide by heating with carbon. The author hopes to prove that the so-called cyanide and nitride of

tilanium is merely a mixture in variable proportions of nitride and carbide.

W. R.

## Action of Organic Acids on Potassium and Sodium Tungstates. By J. LEFORT (Compt. rend., lxxxii, 1182—1185).

SODIUM tungstate has an alkaline reaction to litmus paper; if a solution of the neutral salt be saturated with acetic, oxalic, tartaric, or citric acid, a bitungstate is formed, half the sodium combining with the organic acid. With acetic acid three different salts were obtained; *sodium bitungstate*, in long prisms, of the formula $Na_2O.2WO_3.6H_2O$, by saturating a cold aqueous solution of neutral sodium tungstate with glacial acetic acid; *intermediate sodium tungstate*, prepared by pouring the solution of the tungstate into acetic acid; it forms oblique prisms, and has the formula $2Na_2O.5WO_3.11H_2O$, and lastly sodium tritungstate, formed by pouring a strong solution of the bitungstate into boiling glacial acetic acid; it crystallises in long prisms, and has the formula $Na_2O.3WO_3.4H_2O$. Tungstic acid is not formed by boiling any one of these salts with excess of glacial acetic acid. Similar potassium tungstates were prepared by the same method.. The bitungstate is at first an amorphous precipitate, and has the formula $K_2O.2WO_3.2H_2O$; but when recrystallised from boiling water, it forms nacreous scales with $3H_2O$. The intermediate salt crystallises in prismatic tables; and the tritungstate in fine needles. Tartaric acid appears to form double salts, which were not obtained in a crystalline form, but citrotungstate of sodium, $Na_2O.2WO_3 + Na_2O$, crystallises in beautiful oblique prisms.

Tungstic acid is precipitated by oxalic acid from a hot concentrated solution of sodium tritungstate.

W. R.

## An Explanation of the Strength of Puddled Iron. By H. LE CHATELIER (Compt. rend., lxxxii, 1057—1058).

THE author passed chlorine over a piece of puddled iron, and after the iron, and other metals and metalloïds had volatilised as chlorides, a residue of silica, of the same form as the iron was left, which could be blown away by the slightest breath. It had a definite structure; all the fibres lay in the direction of the length of the iron, and were parallel to each other. The *grain* of iron is produced by the formation of a fusible silicate which penetrates the iron throughout its whole mass, but when the iron is puddled the silica is infusible, and is drawn into filaments which prevent the contact of the fibres of iron with each other; they have more strength therefore to resist a pull. The degree of strength depends on the temperature at which the iron has been puddled.

W. R.

**On Osmium.** By H. SAINTE-CLAIRE DEVILLE and H. DEBRAY (Compt. rend., lxxxii, 1076—1078).

OSMIUM is a beautiful blue metal with a tinge of grey, and the light reflected several times from its surface has a violet colour. It crystallises in agglomerations of cubes or rhombohedrons resembling cubes. It is harder than glass, which it easily scratches. Its density is 22·477.

Metallic osmium is prepared by passing osmic acid, in a current of nitrogen, over finely divided carbon, resulting from the decomposition of benzene by heat: the carbon is oxidised to carbonic oxide, while some of the osmic acid condenses in the cooler part of the tube, and is reduced by the carbonic oxide. A tube of osmium resembling a zinc tube, is formed.

A substance crystallising in scales, having a fine copper-red colour, is sometimes formed, and results from the action of osmium on excess of osmic acid. It is a sesquioxide, stable in the air, having the formula $Os_2O_3$.

Amorphous osmium is prepared by passing osmic acid through a red-hot porcelain tube, together with the mixture of carbonic oxide and anhydride resulting from the decomposition of oxalic acid. It can be crystallised from molten tin; the tin is dissolved with hydrochloric acid, leaving minute crystals of osmium.

W. R.

# Organic Chemistry.

## Formulation of the Paraffins and their Derivatives.

By WM. ODLING (Phil. Mag. [5], i, 205—218).

SCHORLEMMER has already shown that the various modes of arrangement of the marsh-gas residues, which unite to form a paraffin or hydrocarbon of the series $C_nH_{2n+2}$, are reducible to four, namely, a dimethyl sub-class typified by the hydrocarbon, $H_2C\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.$; a tri-methyl sub-class typified by the hydrocarbon, $HC\left\{\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right.$; a tetra-methyl sub-class (A) typified by the hydrocarbon, $C(CH_3)_4$, and another tetra-methyl sub-class (B) exemplified by the compound, $\begin{matrix}HC(CH_3)_2\\|\\HC(CH_3)_2\end{matrix}$: of these, the two former classes are the most important, the members of the two latter being comparatively unknown.

The di- and tri-methylated paraffins have generally been distinguished by the terms *normal* and *iso*-paraffins respectively; the author now proposes to name the two remaining classes, and adopts for the tetra-class (A) the term *neo*-paraffin, and for the tetra-class (B) the term *meso*-paraffin. He further suggests that the letters $\sigma$, $\nu$, and $\mu$

shall be taken as indices of the iso-, neo-, and meso-paraffins, so that the formulæ of the hydrocarbons may be shortly written, as in the following example:—

| $C_6H_{14}$ Hexane. | $C_6H_{14}^{\sigma}$ Isohexane. | $C_6H_{14}^{\nu}$ Neohexane. | $C_6H_{14}^{\mu}$ Mesohexane. |
|---|---|---|---|
| $H_2C\left\{\begin{matrix}C_4H_9\\CH_3\end{matrix}\right.$ | $HC\left\{\begin{matrix}C_3H_7\\CH_3\\CH_3\end{matrix}\right.$ | $C\left\{\begin{matrix}C_2H_5\\CH_3\\CH_3\\CH_3\end{matrix}\right.$ | $\begin{matrix}HC\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.\\ \vert \\ HC\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.\end{matrix}$ |

Notwithstanding that it is possible and sometimes even desirable to write the formula of a paraffin in such a manner as not to express directly that it may be considered as a derivative of methane, yet it will be found that the latter method is more generally advantageous, as it illustrates clearly the relationship of the paraffins between themselves, and the relationship of the normal paraffins to their derived ketones and secondary alcohols.

The study of the reactions of the isomerides produced by the substitution of Cl, OH, or other univalent residue for one proportion of hydrogen in a paraffin, has shown that the isomerism may be fairly considered to result from the introduction of the substituting radicle either for the hydrogen of a methyl residue, or for a methylene or a formyl residue in the original paraffin, and the univalent but differing hydrocarbon-radicles thus resulting, have been spoken of as primary, secondary, and tertiary radicles respectively. It is proposed to retain the terms primary, isoprimary, &c., in their original signification, but to substitute the terms *pseudo*-radicles and *kata*-radicles for secondary and tertiary radicles; thus, adopting as before the letters $\pi$ for pseudo-$\psi$ for pseudiso- and $\kappa$ for kata-radicles, their names and formulæ will appear—

| | Pentyl. | Isopentyl. | Neopentyl. |
|---|---|---|---|
| Primary .. | $H_2C\left\{\begin{matrix}C_3H_6X\\CH_3\end{matrix}\right.$ | $HC\left\{\begin{matrix}C_2H_4X\\CH_3\\CH_3\end{matrix}\right.$ | $C\left\{\begin{matrix}CH_2X\\CH_3\\CH_3\\CH_3\end{matrix}\right.$ |

| | Pseudopentyl ($C_5H_{11}^{\pi}$.) | Pseudisopentyl ($C_5H_{11}^{\psi}$.) |
|---|---|---|
| Pseudo .. | $XHC\left\{\begin{matrix}C_3H_7\\CH_3\end{matrix}\right.$ | $HC\left\{\begin{matrix}CHX.CH_3\\CH_3\\CH_3\end{matrix}\right.$ |

| | Katapentyl ($C_5H_{11}^{\kappa}$). |
|---|---|
| Kata .. ... | $XC\left\{\begin{matrix}C_2H_5\\CH_3\\CH_3\end{matrix}\right.$ |

The relation of the secondary alcohols to the normal paraffins, and of the tertiary alcohols to the isoparaffins is also clearly demonstrated by adopting the foregoing method of notation.

| Normal paraffin. | Primary alcohol. | Secondary alcohol. |
|---|---|---|
| $H_2C\left\{\begin{matrix}C_3H_7\\CH_3\end{matrix}\right.$ | $H_2C\left\{\begin{matrix}C_3H_6.OH\\CH_3\end{matrix}\right.$ | $HO.HC\left\{\begin{matrix}C_3H_7\\CH_3\end{matrix}\right.$ |
| **Isoparaffin.** | **Isoprimary alcohol.** | **Tertiary alcohol.** |
| $HC\left\{\begin{matrix}C_2H_5\\CH_3\\CH_3\end{matrix}\right.$ | $HC\left\{\begin{matrix}C_2H_4.OH\\CH_3\\CH_3\end{matrix}\right.$ | $HO.C\left\{\begin{matrix}C_2H_5\\CH_3\\CH_3\end{matrix}\right.$ |

With respect to the nomenclature of the alcohols, the writer thinks it preferable to restrict the use of the term *carbinol* to the tertiary alcohols; to accord the term pseudo-alcohol or *pseudol* to the secondary alcohols, and to employ the term alcohol specifically to designate the alcohols proper as primary alcohols, which may perhaps be also termed *methols*.

| | Propyl Alcohol or Ethyl Methol. | Isobutyl Alcohol or Pseudopropyl Methol. |
|---|---|---|
| Primary .... | $H_2C\left\{\begin{matrix}CH_2.OH\\CH_3\end{matrix}\right.$ | $HC\left\{\begin{matrix}CH_2OH\\CH_3\\CH_3\end{matrix}\right.$ |
| | **Pseudol.** | **Ethyl-methyl Pseudol.** |
| Secondary | $HO.HC\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.$ | $HO.HC\left\{\begin{matrix}C_2H_5\\CH_3\end{matrix}\right.$ |
| | **Trimethyl Carbinol.** | **Ethyl-dimethyl Carbinol.** |
| Tertiary .. | $HO.C\left\{\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right.$ | $HO.C\left\{\begin{matrix}C_2H_5\\CH_3\\CH_3\end{matrix}\right.$ |

A few words are added respecting the adaptability of the proposed system to the corresponding fatty acids, which however it is unnecessary to reproduce, as it follows as a necessary consequence on a correct appreciation of the notation for the primary alcohols; and with regard to the choice of distinctive names indicative of the modes of origin and transformation of the different isomeric acids, those chemists who use Kolbe's nomenclature will most advantageously employ those names which call to mind that the normal-, iso-, and neo-acids are mono-, di- and tri-methyl, &c., derivatives. Thus we have—

Pentoic or methyl-butyric acid, $H_2C\left\{\begin{matrix}C_2H_4.CO_2H\\CH_3\end{matrix}\right.$.

Isopentoic or dimethyl-propionic acid, $HC\left\{\begin{matrix}CH_4.CO_2H\\(CH_3)_2\end{matrix}\right.$.

Neopentoic or trimethyl-acetic acid, $C\left\{\begin{matrix}CO_2H\\(CH_3)_3\end{matrix}\right.$.

Such terms, however, as butyl-formic, $C_4H_7.CO_2H$, isobutyl-formic, $C_4H_7^{\sigma}.CO_2H$, and katabutyl-formic acids, $C_4H_7^{\kappa}.CO_2H$, express very concisely the relationship of the acids to their corresponding alcohols and carbinols.

J. W.

**Action of Antimony Pentachloride on some Organic Compounds.** By C. W. LÖSSNER (J. pr. Chem. [2], xiii, 418—436).

THE author has investigated the action of antimony pentachloride on various organic bodies, with the following results:—

*Chloroform.*—When equal numbers of molecules of chloroform and antimony pentachloride are gently heated together in a retort or, better, heated to 100° in sealed tubes, the chloroform is converted into carbon tetrachloride, as shown by the equation—

$$SbCl_5 + CHCl_3 = SbCl_3 + CCl_4 + HCl.$$

*Ethyl bromide* is attacked by antimony pentachloride when mixed with it: the whole of the bromine is eliminated and ethyl chloride formed.

*Ethene bromide* is readily acted on by antimony pentachloride. When equal numbers of molecules of the two bodies are mixed together, the chief product is ethylene chlorobromide, the formation of which may be represented thus:—

$$SbCl_5 + 2C_2H_4Br_2 = SbCl_3 + 2C_2H_4ClBr + 2Br.$$

With two molecules of the pentachloride to one of ethene bromide, the product is ethene chloride:

$$SbCl_5 + C_2H_4Br_2 = SbCl_3 + C_2H_4Cl_2 + 2Br.$$

Ethene bromide is not acted on when similarly treated with phosphorus pentachloride.

*Acetic Acid.*—When this substance is added gradually to an equivalent quantity of antimony pentachloride, the mixture becomes hot, and evolves hydrochloric acid. The product of the reaction is monochloracetic acid, accompanied, however, by another substance of higher boiling-point.

*Succinic acid* yields no definite products by its reaction with antimony pentachloride.

*Benzene* reacts with antimony pentachloride to form monochloro- and dichloro-benzene.

*Benzoic acid* yields substitution-products, one, two, or more atoms of hydrogen being replaced by chlorine.

*Phenol* added drop by drop to antimony pentachloride is violently acted on and completely decomposed. No chlorinated phenol is formed. Phosphorus pentachloride reacts with phenol to form chlorobenzene, $C_6H_5Cl$, the result of an exchange of chlorine for hydroxyl.

*Salicylic acid*, when gradually added to antimony pentachloride, yields, amongst other products, monochloro- and dichloro-salicylic acid:

$$SbCl_5 + C_6H_4.COOH.HO = HCl + C_6H_3Cl.COOH.HO + SbCl_3;$$
$$2SbCl_5 + C_6H_4.COOH.HO = 2HCl + C_6H_2Cl_2.COOH.HO + 2SbCl_3.$$

Monochlorosalicylic acid, which is formed in small quantity only, crystallises in small white needles, which melt at 163° and dissolve in hot water, alcohol, and ether. It does not sublime undecomposed.

Dichlorosalicylic acid, on prolonged boiling with potash, exchanges its chlorine for hydroxyl, thus yielding gallic acid, which is accompanied, however, by pyrogallic and oxysalicylic acids.

*Paraoxybenzoic acid*, gently heated with 2 mol. of antimony pentachloride, yields the monochlorinated acid, $C_6H_3Cl.COOH.HO$, which crystallises in white needles melting at 169°—170°, and sublimes without much decomposition. The dichlorinated acid is obtained by treating paraoxybenzoic acid with a larger proportion (4 mol.) of antimony pentachloride, or treating the monochlorinated acid afresh with 2 mol. of the pentachloride. It forms tufts of small needles, which melt at 225°—226°, and sublime without decomposition.

*Oxybenzoic acid* behaves very differently, yielding only resinous products, which it was found impossible to purify.

It is evident from the foregoing facts that the action of antimony pentachloride on organic compounds is totally different from that of phosphorus pentachloride. The action of phosphorus pentachloride on acids results chiefly in the replacement of the hydroxyl-group by chlorine, with simultaneous formation of phosphorus oxychloride, whilst antimony pentachloride simply parts with chlorine, which replaces hydrogen in the acid radicle. In its action on hydrocarbons, ethylene bromide, &c., antimony pentachloride behaves like free chlorine, and it is probable that its energetic action is due to the circumstance that it is easily resolved into trichloride and chlorine, which latter may act in the nascent state upon bodies in contact with it.

J. R.

## Action of Bromine on Ethene Chlorhydrate.

By E. Demole (Deut. Chem. Ges. Ber., ix, 555—562).

When ethene chlorhydrate is heated with bromine for three hours to 130°—140°, it yields water, hydrochloric acid, hydrobromic acid, ethene chlorobromide boiling at 107°—109°, a large quantity of ethene dibromide, ethene bromhydrate and a liquid boiling at 230°—240°, which appears to be ethene acetobromhydrate, as caustic potash resolves it into ethene oxide, hydrobromic acid and acetic acid. The aqueous solution contains bromacetic and dibromacetic acids.

When ethene chlorhydrate is heated with less than one molecule of hydrobromic acid, $HBr + 5H_2O$, for 6—10 hours to 160°—170°, it yields a large proportion of ethene dichloride and smaller quantities of ethene chlorobromide, dibromide and bromhydrate. If equal molecules are heated to 140° the same products are formed, but the dibromide and chlorobromide preponderate.

On heating one part of chloracetic acid with two parts of the aqueous hydrobromic acid, bromacetic acid and other products are formed.

C. S.

**Simple Preparation of Propene.** By A. CLAUS (Deut. Chem. Ges. Ber., ix, 695—696).

WHEN dichlorhydrin is distilled over zinc-dust, hydrogen and propene are formed; the same products are obtained when concentrated glycerin is mixed with so much zinc-dust that a thick paste is formed, and the mixture is heated. 100 grms. of glycerin gave 35—40 litres gas, of which one-half consisted of propene. Other products, as a yellow volatile oil and resinous bodies, are formed at the same time.

C. S.

**Products obtained by the Action of Hypochlorous Acid upon Non-saturated Compounds, particularly Propene.** By LOUIS HENRY (Bull. Soc. Chim. [2], xxv, 388—389).

THE author maintains, in contradiction to Markownikoff, that the product $C_3H_6Cl(OH)$ has the constitution $CH_2OH—CHCl—CH_3$, because he obtained from it chloropropionic acid, by oxidation with nitric acid. Markownikoff insists, however, that the following formula is the correct one, viz., $CH_2Cl—CHOH—CH_3$, as he obtained monochloracetic acid, and finally acetic acid, on oxidising this compound with chromic acid. The author contends that the experiments of Markownikoff prove nothing, as the reducing properties of monochloracetone and monochloropropionic aldehyde should be identical, as also their boiling points; further, he has proved that chloropropionic acid furnishes acetic acid, on being oxidised by chromic acid. The chlorhydrate, $CH_2Cl—CH(OH)—CH_3$, produced by the action of sulphuric acid on allyl chloride, gives monochloracetic acid on being oxidised by nitric acid, from which it is apparent that it differs completely from the compound obtained by the action of hypochlorous acid upon propene.

C. A. B.

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**Preparation of Glycol.** By E. DEMOLE (Deut. Chem. Ges. Ber., ix, 636).

IN a recent paper on this subject, Börnstein stated that he had failed to obtain glycol by Demole's process. The author attributes the failure to the circumstance that Börnstein neglected to dry the potassium acetate used in the process.

J. R.

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**Specific Rotatory Power of Grape Sugar.** By B. TOLLENS (Deut. Chem. Ges. Ber, ix, 487—494).

THIS paper contains the results of numerous experiments on the specific rotatory power of pure grape sugar prepared by several processes, and examined by various polarising instruments. The result arrived at by the author is that for pure anhydrous grape sugar, in solutions containing 3 grms. or more in 100 c.c., $\alpha_y = 53{\cdot}10$ with yellow light: for $C_6H_{12}O_6 + H_2O$, $\alpha_y = 48{\cdot}27$.

J. R.

**Additive Products of Aldehyde.** By R. SCHIFF (Deut. Chem. Ges. Ber., ix, 565—574).

ALDEHYDE-AMMONIA acts on the mustard-oils (sulphocarbimides), the reaction being complete if two molecules of the former to one of the latter is used.

On using phenylic sulphocarbimide, and heating the substances in presence of a large quantity of absolute alcohol until the sulphocarbimide has disappeared, the solution solidifies on cooling to a crystalline mass, which crystallises from hot alcohol in glistening silver-white needles, melting at 148°, and decomposing when more strongly heated; its composition is $C_{22}H_{31}N_5O_2S_2$, and it is formed according to the equations:—

$$2C_2H_7NO + C_7H_5NS = C_{11}H_{17}N_3OS + H_2O.$$
$$2C_{11}H_{17}N_3O_2S = C_{22}H_{31}N_5OS_2 + NH_3.$$

It dissolves in:—

| | Cold. | Hot. |
|---|---|---|
| Water ..... | Scarcely | Moderately |
| Alcohol ..... | Sparingly | Freely |
| Ether ..... | Not | Very sparingly |
| Carbon sulphide .... | Sparingly | Sparingly |
| Benzene ..... | Not | Very sparingly |
| Chloroform ..... | Freely | Very freely. |

It has a very bitter taste, like quinine sulphate. It is slowly decomposed by boiling water, more quickly by alkalis and acids. When hydrochloric acid is passed into its solution in chloroform, a hydrochloride is precipitated as a gelatinous mass, and on heating the body with aqueous hydrochloric acid to 150°, it is resolved into aldehyde, hydrogen sulphide, carbon sulphide, ammonia, and aniline.

When added to acetic anhydride, which is heated on a water-bath, it is resolved into aldehyde and acetophenylthiosinnamine, $CS\left\{\begin{matrix}NH(C_6H_5)\\NH(C_2H_3O)\end{matrix}\right.$, which crystallises from alcohol in iridescent plates melting at 173°.

When common mustard oil (allyl-sulphocarbimide) is heated with aldehyde-ammonia in presence of alcohol, the compound $C_{16}H_{31}N_5O_2S_2$ is formed, which dissolves freely in alcohol, chloroform, and hot water. It is much more unstable than the phenyl-compound, and forms a hydrochloride crystallising in microscopic needles. On heating a larger quantity with water, the liquid leaves on evaporation a syrupy mass, which on standing, and more quickly on adding dilute sulphuric acid, yields thiosinnamine.

Ethylic sulphocarbimide yields the compound $C_{14}H_{31}N_5O_2S_2$, crystallising in glistening silver-white, large needles, melting at 118°—119°, and possesses properties analogous to those of the preceding compounds.

C. S.

## Electrolysis of Oxalic Acid. By M. Bunge (Bull. Soc. Chim. [2], xxv, 393).

Aqueous solutions of oxalic acid were decomposed by electrolysis, when it was observed that hydrogen was evolved at the negative pole, and carbonic acid gas and oxygen at the positive pole. The quantity of oxygen is directly proportionate to the strength of the current, the strength of the solution, and the temperature. The amount of carbonic acid gas evolved increases as the quantity of oxygen decreases.

C. A. B.

## Dry Distillation of Tartaric Acid. By C. Böttinger (Deut. Chem. Ges. Ber., ix, 670—673).

The decomposition of tartaric acid, when distilled under proper conditions, is in accordance with the equation:—

$$C_4H_6O_6 = C_3H_4O_3 + CO_2 + H_2O,$$

and is analogous to the formation of citraconic and itaconic acids from citric acid:—

$$C_6H_8O_7 = C_5H_6O_4 + CO_2 + H_2O.$$

Glyceric acid would seem to be formed as an intermediate step, and as it is decomposed at 140°, with formation of peculiar, probably anhydride-like bodies, the pyruvic acid may owe its origin to a body formed both from tartaric and glyceric acids.

If a mixture of powdered tartaric acid with excess of barium hydrate is exposed for a week to a temperature of 100°—110°, carbonic acid is separated, and peculiar products soluble in ether, and with an unpleasant smell, are formed, but no glyceric acid.

G. T. A.

## Normal Pyrotartaric Acid. By M. Reboul (Bull. Soc. Chim. [2], xxv, 386—388).

Normal pyrotartaric acid ($CO_2H.CH_2—CH_2—CH_2.CO_2H$) is obtained by heating propene dicyanide ($CN.CH_2—CH_2—CH_2.CN$) with about one and a half times its volume of concentrated aqueous solution of hydrochloric acid in a sealed tube, from three to four hours at 100° C. The mixture almost solidifies on cooling. The contents of the tube are then evaporated down on a water-bath, treated with absolute alcohol in order to separate the ammonium chloride, and the alcoholic solution is evaporated down, when the acid is left behind as a thick brown syrup which crystallises very slowly. This syrup is then carefully neutralised with barium hydrate, and the neutral barium pyrotartrate solution thus formed is concentrated, whereupon the salt separates out in needles on cooling. The pure salt has the formula $C_5H_6O_4Ba + 5H_2O$. It loses the five molecules of water on being heated to 135°, is very soluble in water (particularly hot water) and

insoluble in alcohol, which precipitates it from its aqueous solutions. Normal pyrotartaric acid is easily obtained by treating the above-mentioned barium salt with the equivalent amount of dilute sulphuric acid, separating the resulting barium sulphate precipitate, and evaporating the solution down. The acid thus obtained melts at about 103° to 104°, and when treated with silver nitrate, forms a slightly flocculent white precipitate of silver pyrotartrate ($C_5H_6O_4Ag_2$), which blackens rapidly in the light and is difficult to wash. If this silver salt be suspended in water, and a current of sulphuretted hydrogen gas passed through it, the same time normal pyrotartaric acid is obtained, having, however, a melting point of 97°, which appears to be the normal melting point of the pure acid. The two isomerides of normal pyrotartaric acid, and the ethyl-malonic acid of Wislicenus, melt at 111°—112°. Water, alcohol, and absolute ether dissolve normal pyrotartaric acid easily.

C. A. B.

## On Synthetical Pyrotartaric Acid. By A. Lebedeef (Bull. Soc. Chim. [2], xxv, 395).

In studying the isomerism of ordinary pyrotartaric acid and the acid obtained synthetically by Simpson from bromide of propylene, the author observed that the destructive distillation of the synthetically obtained acid resulted in the formation of an anhydride, boiling at 244·9°. Simpson states that he obtained only water and an oil not exhibiting any acid reaction. The author prepared the neutral ammonium and calcium salts of the synthetical acid.

C. A. B.

## Methazonic Acid.

By M. T. Lecco (Deut. Chem. Ges. Ber., ix, 705—707).

This acid, discovered by Friese, is best prepared by dissolving four grms. of caustic soda in hot alcohol and adding five grms. of nitromethane drop by drop. The liquid is then boiled for a short time, and after cooling, the salt which has separated is filtered off, dissolved in water, and decomposed by dilute sulphuric acid. On shaking the liquid with ether, the methazonic acid is dissolved; the solution is dried over anhydrous Glauber salt and then evaporated over sulphuric acid. A yellow syrup is left behind, which, on standing, is converted into large crystals, mixed with a thick reddish syrup, which colours the skin intensely red. To purify the body it is pressed between paper and crystallised from warm benzene.

Methazonic acid, $C_2H_4N_2O_3$, is isomeric with ethylnitrolic acid and is an unstable body, which decomposes spontaneously and assumes a red colour. It is readily soluble in water, alcohol, and ether, more sparingly in benzene and not in petroleum-naphtha. On heating, it softens and liquefies at 58°—60°; when more strongly heated it explodes.

The sodium salt crystallises from dilute alcohol in long prisms and is more explosive than the acid; the methazonates of the heavy metals

are obtained by precipitation. The formation of methazonic acid is explained by the equation:

$$2CH_3NaNO_2 = NaOH + C_2H_3NaN_2O_3.$$

It is perhaps a kind of anhydride of nitromethane: $\left.\begin{matrix}CH_2NO\\CH_2NO\end{matrix}\right\}O.$

C. S.

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**Dinitrobutane.** By V. MEYER (Deut. Chem. Ges. Ber., ix, 701—705).

SECONDARY nitrobutane yields a butylpseudonitrol, which, like other pseudonitrols, is converted by heat or oxidation into the dinitro-compound $CH_3.CH_2.C(NO_2)_2.CH_3$, a colourless, mobile oil, having an agreeable smell, and boiling at 199° with slight decomposition. It is insoluble in potash, and is resolved by the action of tin and hydrochloric acid into methyl-ethyl ketone and hydroxylamine.

C. S.

**Structure of Cyanic and Cyanuric Acids.** By A. CLAUS (Deut. Chem. Ges. Ber., ix, 721—724).

THE author maintains, against Nencki, Weith, and Fleischer, that cyanic and cyanuric acids are not imido-compounds but contain hydroxyl.

C. S.

**Constitution of Cyanic Acid.** By W. MICHLER (Deut. Chem. Ges. Ber., ix, 715—716).

WHEN unsymmetrical diphenyl-urea, $C_6O\left\{\begin{matrix}NH_2\\N(C_6H_5)_2\end{matrix}\right.$, is distilled, it is resolved into diphenylamine and cyanic acid, and triphenyl-urea yields, under the same conditions, phenyl cyanate and diphenylamine. From these reactions it appears that cyanic acid has the constitution $HN{=}C{=}O$.

C. S.

**Constitution of the Fulminates.** By A. STEINER (Deut. Chem. Ges. Ber., ix, 779—787).

FURTHER examination of the substance formed by the action of dry hydrogen sulphide on dry mercuric fulminate (see this Journal, 1876, i, 378), has shown that it consists of fulminic acid combined with hydrogen sulphide:

$$C_2H_2N_2O_2 + H_2S = C_2H_4N_2O_2S.$$

It forms microscopic prisms, insoluble in water but moderately soluble in alcohol and ether, from which they can be recovered only by spontaneous evaporation, since they decompose below the boiling-point of ether. They explode below 100°, leaving sulphur.

*Fulminuric Acid.*—In a former paper the author showed that mercuric fulminate, when treated with aqueous ammonia, yields urea and guanidine. Alcoholic ammonia, he now finds, acts in an entirely different manner, the products being ammonium carbonate and fulminuric acid in the form of a basic mercury compound.

Fulminuric acid, when treated with strong sulphuric acid, evolves carbon dioxide and yields *nitracetonitril*, $C_2H_2N_2O_2$, a body forming colourless transparent crystals which melt at about 40°, volatilise readily, dissolve easily in ether and alcohol, and burn with a brilliant flame.

Nitracetonitril gives with mercuric nitrate a precipitate of the compound $(C_2HN_2O_2)_2Hg$, which explodes when heated.

*Double Salts of Mercuric Fulminate.*—$C_2HgN_2O_2 + CNK$ is obtained by adding mercuric fulminate to a warm solution of potassium cyanide. It crystallises in needles, which are soluble in cold water and alcohol. On adding dilute acids to its solution, pure mercuric fulminate is thrown down as a snow-white crystalline powder. $C_2HgN_2O_2 + CNSK$ is formed when mercuric fulminate is added to a warm solution of potassium sulphocyanate. It crystallises in laminæ.

J. R.

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## On the Behaviour of Cyanamide, Dicyanodiamide, and Melamine under the Action of Heat. By E. Drechsel (J. prakt. Chemie [2], xiii, 330—333).

The author stated in his previous communication on cyanamide (*J. prakt. Chemie* [2], 11, 284), that dicyanodiamide when cautiously heated partially sublimes undecomposed. In support of this assertion he relied upon the behaviour of the aqueous solution of the sublimate with silver nitrate. He did not consider the probability of the sublimate in question containing melamine, since Liebig asserted (*Ann. Chem. Pharm.*, x, 19) that this substance could not be sublimed. He, however, recently observed that on cautiously heating pure melamine, a sublimate was obtained corresponding exactly with melamine itself. From this observation he was led to institute fresh experiments on the behaviour of these bodies under the action of heat.

*Cyanamide* is converted only into dicyanodiamide. If a small quantity be heated in a tube it begins to decrepitate, but if the tube be removed from the source of heat, an energetic reaction sets in; ammonia is developed, and in the farthest part of the tube some cyanamide condenses; but the principal products of the reaction are a sublimate, at first oily, but rapidly crystallisable, consisting of dicyanodiamide, and a yellowish residue of melam. The dicyanodiamide was recognised not merely by its reaction with silver, but also by first converting it into dicyanodiamidine, and then testing for this latter substance by means of copper solution and concentrated soda lye. This reaction is very delicate even in the presence of a moderately large quantity of melamine.

*Dicyanodiamide* melts when heated and evolves ammonia gas. On heating it still more strongly, a white crystalline sublimate forms, ammonia gas escapes, and a yellowish residue is left behind. This

residue is not dicyanodiamide, but almost pure melamine. On heating dicyamindiamide quickly and strongly, a reaction sets in similar to that with cyanamide, and the resulting white sublimate contains cyanamide and melamine, but no dicyanodiamide.

*Melamine* furnishes a crystalline sublimate when heated in a tube; at a higher temperature it melts and decomposes exactly as asserted by Liebig, but at a temperature slightly below its melting point it sublimes unchanged.

The author takes this opportunity of remarking that melamine sulphate can be crystallised with different proportions of water of crystallisation, but notwithstanding many experiments, he has not been quite successful in preparing precisely either the salt $(C_3N_6H_6)_2H_2SO_4 + 2H_2O$ or $2(C_3N_6H_6)_2H_2SO_4 + 3H_2O$.

H. H. B. S.

## Substituted Ureas.

By W. MICHLER (Deut. Chem. Ges. Ber., ix, 710—714).

WHEN the chloride $Cl.CON(C_6H_5)_2$, which the author obtained by passing carbonyl chloride into a solution of diphenylamine in chloroform, is heated with diphenylamine to 200°—220°, *tetraphenyl-urea*, $CO[N(C_6H_5)_2]_2$, is formed. It is freely soluble in boiling alcohol, and forms yellowish crystals melting at 183°. When heated with hydrochloric acid to 250°, it is resolved into carbon dioxide and diphenylamine.

When diethylamine is added to a solution of the chloride of phenylcarbamide in chloroform, a violent reaction sets in, and *diphenyldiethylurea*, $CO\left\{\begin{matrix}N(C_6H_5)_2\\N(C_2H_5)_2\end{matrix}\right.$, is formed. It crystallises from alcohol in plates melting at 54°, and having a peculiar smell. On distilling it with potash it is resolved into carbon dioxide, diphenylamine, and diethylamine.

An isomeride is obtained by saturating ethylaniline with phosgene, and heating the chloride thus formed with an equal volume of ethylaniline to 130°. This *symmetrical* urea, $CO\left\{\begin{matrix}N\left\{\begin{matrix}C_2H_5\\C_6H_5\end{matrix}\right.\\N\left\{\begin{matrix}C_2H_5\\C_6H_5\end{matrix}\right.\end{matrix}\right.$, separates from alcohol in crystals melting at 79°.

*Triphenylethyl urea*, $CO\left\{\begin{matrix}N\ (C_6H_5)_2\\N\left\{\begin{matrix}C_2H_5\\C_6H_5\end{matrix}\right.\end{matrix}\right.$, is formed by heating ethylaniline with the chloride of diphenyl carbamide; it crystallises from alcohol in needles.

All these ureas, with the exception of the symmetrical diphenyldiethyl urea, give with sulphuric acid the blue reaction of diphenylamine.

*Diphenyltolyl urea*, $CO\left\{\begin{matrix}N(C_6H_5)_2\\NH.C_7H_7\end{matrix}\right.$, is obtained by heating diphenyl carbamide chloride with paratoluidine to 130° for half an hour, whereas on using an excess of toluidine and heating longer, ditolyl

urea and diphenylamine are formed. When diphenyltolyl-urea is heated, it is resolved into carbon dioxide, toluidine, and diphenylamine.

C. S.

## Action of Alcoholic Ammonia on Substituted Ureas.

By A. CLAUS (Deut. Chem. Ges. Ber., ix, 693—695).

BY brominating diphenyl-urea, a dibromo-compound is formed, which, when heated with alcoholic ammonia to 140°—150°, is resolved into 1 mol. of urea and 2 mols. of bromaniline. Under the same conditions diphenyl-urea yields urea and aniline, and diphenylthiourea undergoes an analogous decomposition, but, as might be expected, the greater part of the thiourea is converted into ammonium thiocyanate.

Benzidine urea, $CO\left\{\begin{matrix} NH—C_6H_4 \\ | \\ NH—C_6H_4 \end{matrix}\right.$, which is obtained by heating benzidine with urea and alcohol, is by alcoholic ammonia again resolved into its components.

C. S.

## Formation of Allantoïn from Uric Acid in the Animal Body.

By E. SALKOWSKI (Deut. Chem. Ges. Ber., ix, 719—721).

IN determining urea by Bunsen's method, it must be remembered that also creatinine, creatine, uric acid, uramido-acids, and allantoïn yield ammonium carbonate when heated with an ammoniacal solution of barium chloride, and allantoïn gives also oxalic acid; but none of these compounds give $2NH_3$ for $1CO_2$, and if, therefore, this proportion is not found, other bodies besides urea must be present. In examining urine, the author uses the following modification of Bunsen's method. One litre of a saturated solution of barium chloride is mixed with 15—20 c.c. of soda solution of 30 per cent. Equal volumes of this liquid and urine are mixed, filtered after a few minutes, and in 15 c.c. of the filtrate the free alkali is determined by $\frac{1}{10}$ standard acid, while another 15 c.c. are sealed up and heated for four hours to 220°—230°. The contents of the tube are then filtered, the barium carbonate is washed, dried, and weighed, and in a portion the carbon dioxide is determined, while another portion is examined for oxalic acid. In the filtrate and wash-water the free alkali is determined, and then it is evaporated with a few drops of acid, and the residue distilled with potash to determine the ammonia.

The author found that usually the urine after heating with the alkaline solution of barium chloride, required 2—2·5 c.c. less of the standard acid than before, which is partly due to an unavoidable loss of ammonia, but also probably to the formation of some acid.

On feeding a dog with uric acid, it was found that the difference in the alkalescence increased to 6—7 c.c., which pointed to the presence of allantoïn in the urine, and indeed it could be easily isolated. The urine of a dog which during two days got 8 grms. of uric acid, yielded 1·42 grm. of allantoïn. Only a small quantity of oxalic acid was present,

and of uric acid only a trace. According to Claus, 3 mol. of allantoïn give $12NH_3$, $6CO_2$, 2 oxalic acid, and 1 acetic acid, or the acids formed by 3 mols. of allantoïn correspond to 5 mols. of NaOH. The author's own experiments, however, showed that the acids formed from 0·01 grm. of allantoïn correspond to 1 c.c. of the $\frac{1}{10}$ standard acid.

C. S.

## On the Reducing Action between Sugar and Uric Acid.

By J. SEEGER (Chem. Centr., 1875, 361).

THE author states that even in the cold a mixture of uric acid and sugar will appreciably reduce an alkaline copper solution (Fehling solution), though sugar alone effects a scarcely appreciable reduction.

E. N.

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## On Acetylpersulphocyanic Acid.

By P. DE CLERMONT (Compt. rend., lxxxii, 1103—1105).

WHEN persulphocyanic acid is boiled with acetic anhydride, it slowly dissolves with a brown colour, and on cooling, yellow needles of the above-mentioned compound are deposited. It has the same composition and properties as the acetylpersulphocyanic acid which Nencki and Leppert obtained by acting on ammonium sulphocyanate with acetic anhydride or glacial acetic acid.

It gives with copper a compound of an olive-green colour, the formula of which is—

$$(C_2H.C_2H_3ON_2S_3)_2Cu_2 + CuO.$$

Reducing agents convert it into thiourea.

Persulphocyanic acid, heated in a sealed tube with glacial acetic acid to 140°, is decomposed into sulphur, sulphuretted hydrogen, sulphocyanic acid, and other products.

W. R.

## Regeneration of Diacetonamine from Triacetonamine, and formation of a fifth Acetone-base.

By W. HEINTZ (Liebig's Annalen, clxxxi, 70).

IN the hope of removing the elements of water from triacetonamine, and thus producing a base free from oxygen, viz., dehydrotriacetonamine, $C_9H_{15}N$, the author boiled the substance with excessively concentrated potash and calcium chloride solutions without the slightest result in either case: long-continued heating with absolute alcohol at 100° produced a little decomposition, but not of the desired kind; whilst heating to 100° for 8—16 hours with 8—10 parts fuming hydrochloric acid (sp. gr. 1·17), gave rise to the evolution of no gas, but formed a considerable amount of diacetonamine: if a temperature of 125°—135° be employed little or no triacetonamine remains unaltered. After due purification the diacetonamine thus formed is identical with ordinary diacetonamine, although when it is only approximately pure slight

differences in the appearance of the platinochloride are noticeable. The angles of the crystals of the platinochloride are identical with those of the ordinary diacetonamine salt, whilst the free base and the oxalate agree in water of crystallisation and in all other respects with diacetonamine and its oxalate.

It would hence seem probable that either methylchloracetol or its decomposition-product, monochloropropylene, was formed during the reaction of hydrochloric acid on triacetonamine, but no definite proof of the existence of either substance amongst the products of the change could be obtained; on the other hand a small quantity of a body much resembling mesityl oxide was obtained, apparently formed by the decomposition of a portion of the diacetonamine, as a small quantity of the same substance was produced on heating pure diacetonamine hydrochloride to 130° and more at 180°, ammonia being also produced. Consequently the methylchloracetol or chloropropylene must be supposed to have acted on a portion of the diacetonamine, giving rise to hydrogen chloride and more highly carburised bases. Such bases are indeed present in the products of the reactions, forming a noncrystalline platinum salt after separation of diacetonamine platinochloride by crystallisation. This platinum salt contained 24·72 per cent. of platinum, whilst tetra-acetonamine platinochloride would require 24·60 per cent.

The crude product of the action of hydrochloric acid on triacetonamine allows an oily substance to separate on cooling; this is soluble in ether, and contains a base apparently identical with that which separates as a crystalline hydrochloride from the aqueous liquid to which the ether has been added. These minute crystals when collected and purified by recrystallisation are found to be the hydrochloride of a base, $C_{15}H_{23}N$, formed thus from acetone and ammonia—

$$5C_3H_6O + NH_3 = 5H_2O + C_{15}H_{23}N,$$

just as dehydrotriacetonamine is formed from 3 molecules of acetone and 1 of ammonia by elimination of 3 molecules of water. This base, *dehydropentacetonamine*, constitutes 4—5 per cent. of the products of the action; its hydrochloride is colourless and difficultly soluble in water. On cooling a hot aqueous solution, no crystals separate, but on spontaneous evaporation crystalline crusts appear. Attempts to form this body by the reaction of methylchloracetol or chloropropylene on di- or tri-acetonamine are contemplated. The free base separates as an oil by adding fixed alkalis or ammonia to the hydrochloride; it is noticeable that this base differs from sparteine, $C_{15}H_{26}N_2$, by the elements of 1 molecule of ammonia, and hence by removing ammonia from sparteine dehydropentacetonamine or an isomeride should result.

Attempts to form dehydrotriacetonamine by acting on triacetonamine with sulphuric acid and phosphoric anhydride led to no results; decomposition ensues at 150°—200° with sulphuric acid, but no dehydrotriacetonamine could be obtained from the products of the reaction; much the same remarks apply to the phosphoric anhydride process. It hence results that in order to form dehydrotriacetonamine some peculiar conditions are requisite, and that these are ob-

tained in the process for preparing di- and tri-acetonamine (when dihydrotriacetonamine is formed as a bye product), but were not observed in any of the foregoing experiments.

C. R. A. W.

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**Tetrachlorobenzene.** By F. B. BEILSTEIN and A. KURBATOW (Deut. Chem. Ges. Ber., ix, 579—580).

THIS compound, in which the chlorine occupies the positions 1, 3, 4, 5, was obtained by igniting the platino-chloride of diazotrichlorobenzene from common trichloraniline with soda. It is sparingly soluble in alcohol and crystallises therefrom in needles melting at 50°—51° and boiling at 246°. It dissolves readily in benzene, petroleum-naphtha, and carbon sulphide. With concentrated nitric acid it yields $C_6HCl_4NO_2$, which is readily soluble in benzene, carbon sulphide, and hot alcohol, and crystallises in needles melting at 20°—22°.

In common tetrachlorobenzene the chlorine is in the positions 1, 2, 4, 5, because it is obtained from common trichlorobenzene (1, 3, 4) by converting it first into the mononitro-compound, which on reduction yields the trichloraniline melting at 94°—95°. When the nitro-compound is heated with alcoholic ammonia to 200°, it is converted into a dichloronitraniline crystallising from benzene in long red needles melting at 171°. By the diazo-reaction it is converted into nitro-orthodichlorobenzene melting at 43°.

Tetrachlorobenzene (1, 2, 4, 5) melts at 137°—138° and boils at 243°—246°. It differs from its isomeride by yielding *chloranil* when boiled with nitric acid. This reaction is a further proof that quinone is a para-compound.

C. S.

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**Nitrometachloronitrobenzene and some of its Derivatives.** By AUG. LAUBENHEIMER (Deut. Chem. Ges. Ber., ix, 760—774).

NITROMETACHLORONITROBENZENE is obtained by heating metachloronitrobenzene with excess of fuming nitric and strong sulphuric acids. It is a faintly yellow body, dissolving sparingly in cold alcohol, freely in ether. In contact with the skin it produces painful blisters. It exists in four physically different modifications, three of which ($\alpha$, $\beta$, and $\gamma$) are solid, the other liquid.

The $\alpha$-modification forms thick crystals of the monoclinic system. It melts at 36·3°. In time it becomes transformed into the $\gamma$-modification, this change being accelerated by pressure or trituration.

The $\beta$-modification forms long monoclinic prisms, melting at 37·1°. It likewise passes in time into the $\gamma$-modification.

The $\gamma$-modification crystallises in long, thin, shining needles, which melt at 38·8°.

Either of these modifications can be obtained at will by introducing a crystal of the desired modification into the fused substance or its ethereal solution.

Metachloronitrobenzene exists in two physically different modifica-

tions, one of which melts at 44·2°, the other at 23·7°. The latter is very unstable.

*Derivatives of Nitrometachloronitrobenzene.*—1. When heated with soda-ley it yields chiefly *chloronitrophenol*, according to the equation—

$$C_6H_3Cl(NO_2)_2 + NaOH = C_6H_3Cl(NO_2)OH + NaNO_2.$$

Chloronitrophenol crystallises from water in delicate lemon-yellow prisms, which dissolve easily in alcohol, acetic acid, and ether. It sublimes in long needles, melting at 38·9°. A portion melted in a capillary tube and then cooled with water melts again at 32·7°. The *sodium* and *potassium salts* crystallise in scarlet needles, soluble in water. The *barium salt* forms scarlet, the *calcium* salt yellow needles, sparingly soluble in water. The *lead* salt is a crystalline orange-yellow precipitate; the *silver* salt forms vermilion-red needles: both are very slightly soluble in water.

2. Nitrometachloronitrobenzene reacts with aniline in the cold to form, in the first place, aniline nitrite and *chloronitrodiphenylamine*, thus:—

$$C_6H_3Cl(NO_2)_2 + 2C_6H_5.NH_2 = C_6H_5.NH_2.NO_2H + \begin{matrix}C_6H_3Cl(NO_2)\\C_6H_5\end{matrix}\!\!>\!NH.$$

The aniline nitrite then reacts with another molecule of aniline to form diazodiamidobenzene—

$$C_6H_7N,NO_2H + C_6H_7N = C_6H_5—N_2—NHC_6H_5 + 2H_2O,$$

and the latter, on subsequent treatment of the product with hydrochloric acid, is transformed into *amidoazobenzene*, $C_6H_5—N_2—C_6H_4NH_2$.

Chloronitrodiphenylamine crystallises from alcohol in long red needles, melting at 108·5°. It is insoluble in water and does not combine with acids. When treated with nitrous acid it yields *chloronitrodiphenylnitrosamine*—

$$\begin{matrix}C_6H_3ClNO_2\\C_6H_5\end{matrix}\!\!>\!N(NO),$$

a body crystallising from alcohol in yellow hexagonal laminæ, which melt at 110·5°.

3. Nitrometachloronitrobenzene reacts with tin and hydrochloric acid when boiled therewith. The product is *chlorophenylenediamine*, $C_6H_3Cl(NH_2)_2$, which crystallises from water in small colourless laminæ, melting at 72°. Its aqueous solution gives a white curdy precipitate, which speedily turns red in sunlight, with silver nitrate, a white precipitate with mercuric chloride, and a precipitate of bluish-violet needles with copper sulphate. The *salts* of chlorophenylenediamine are easily soluble in water; they assume a red colour in the air.

Nitrometachloronitrobenzene reacts also with other amines of the fatty and aromatic series and with amides. The investigation is being continued.

J. R.

## Paraoxybenzaldehyde. By R. BÜCKING (Deut. Chem. Ges. Ber., ix, 527—529).

THIS body is obtained by heating anisaldehyde and dilute hydrochloric acid for 3—4 hours to 190°—200°. It forms with acid sodium sulphide a compound which is very soluble in water and crystallises from hot water in radiating, colourless needles, melting at 111°—112° and solidifying at 106°—107°. It has an agreeable aromatic odour, reduces ammonical silver-solutions and forms crystalline alkali-salts. With ferric chloride it gives a dirty violet colour. By fusing it with potash it is converted into paraoxybenzoic acid, which is also formed, but not readily, by oxidising the aldehyde in solution.

C. S.

## Dibromo- and Diiododinitroxysulphobenzide. By J. ANNAHEIM (Deut. Chem. Ges. Ber., ix, 660—662).

IN oxysulphobenzide two of the four hydrogen-atoms in combination with the carbon can be replaced by chlorine, bromine, and iodine, but in methyl- and ethyloxysulphobenzide only one can be replaced by these elements, and on the nitro-derivatives of the latter compounds, *e.g.*, on nitramyloxysulphobenzide the halogens have no action. The substitution of the hydrogen of the hydroxyl by alcohol-radicles has therefore rendered oxysulphobenzide proof against the action of these elements. If this is so, it follows that, as there are a tetrachloro-, bromo-, and iodoxysulphobenzide, only two atoms of hydrogen in dinitroxysulphobenzide—

$$\left.\begin{matrix}C_6H_3NO_2OH\\C_6H_3NO_2OH\end{matrix}\right\}SO_2.$$

can be replaced by chlorine, bromine, or iodine.

Experiments have shown this to be the case, and the following new compounds have been obtained:—

1. Dibromodinitroxysulphobenzide—

$$\left.\begin{matrix}C_6H_2BrNO_2OH\\C_6H_2BrNO_2OH\end{matrix}\right\}SO_2,$$

is prepared by mixing 34 grms. of dinitroxysulphobenzide (to which a little bisulphide of carbon has been added) with 32 grms. of bromine, evaporating to dryness on the water-bath, washing with water, dissolving in sodium carbonate and crystallising out the sodium salt.

Sodium dibromodinitroxysulphobenzide crystallises in small, yellowish-red needles, soluble in hot water, but with some difficulty in cold water. The free acid is separated from the solution on addition of hydrochloric acid. Dibromodinitroxysulphobenzide is insoluble in water, soluble with difficulty in alcohol, but easily soluble in boiling acetic acid, from which it separates again in white needles of a faint straw colour. It melts at 284°—285°.

2. Diiododinitroxysulphobenzide—

$$\left.\begin{matrix}C_6H_2INO_2OH\\C_6H_2INO_2OH\end{matrix}\right\}SO_2,$$

is prepared by bringing together 50 grms. of iodine dissolved in alcohol and a mixture of 34 grms. of dinitroxysulphobenzide with 21·6 grms. of yellow mercuric oxide and heating on the water-bath. After filtration and washing with water, the product is boiled with sodium carbonate and extracted two or three times with boiling water. The difficultly soluble sodium salt separates from the hot solution in fine orange-red needles.

Diiododinitroxysulphobenzide is insoluble in water and alcohol, but dissolves in boiling acetic acid. It melts at 294°—295°. Like the previous compounds, it possesses acid properties and decomposes the alkaline carbonates.

The author is engaged in the preparation of a tetranitroxysulphobenzide.

$$\left.\begin{matrix} C_6H_2(NO_2)_2OH \\ C_6H_2(NO_2)_2OH \end{matrix}\right\} SO_2.$$

G. T. A.

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**Tetraphenylethane and Tetraphenylethene.** By W. STAEDEL (Deut. Chem. Ges. Ber., ix, 562).

THESE two hydrocarbons are formed, together with diphenylmethane, when benzophenone is heated with zinc-dust.

C. S.

**Action of Ammonia on Chloracetylbenzene.** By W. STAEDEL and L. RÜGHEIMER (Deut. Chem. Ges. Ber., ix, 563—564).

THESE bodies act readily on each other, even in the cold, more quickly on heating, and yield different products. One of them has the composition $C_8H_7N$, and crystallises from hot benzene or glacial acetic acid in glistening, serrated plates, melting at 194°—195°, and subliming in pearly plates.

O. Wallach adds to this paper that he has also commenced a similar research, and found that it is best to leave the two bodies in contact in alcoholic ammonia for some time.

C. S.

**New Colouring Matter from Cresol.** By J. ANNAHEIM (Deut. Chem. Ges. Ber., ix, 662).

BY heating cresol with strong sulphuric acid for a few hours to 120°—130° a dark mass is obtained, which dissolves in acetic acid to a fine fuchsine-red. This colour is not affected by acids, but is quickly destroyed by alkalis.

G. T. A.

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**On β-Chlornaphthalene.** By W. RIMARENKO (Deut. Chem. Ges. Ber., ix, 663—666).

β-NAPHTHOL was distilled with an equivalent of phosphorus pentachloride in a retort over an open fire. Water was gradually added to the

distillate and the solid mass obtained was again distilled. The part which passed over between 260° and 275°, when crystallised from alcohol, had the composition $C_{10}H_7Cl$. Its vapour-density was 5·6442.

β-chlornaphthalene is a solid body resembling naphthalene in appearance. It is easily soluble in alcohol, ether, bisulphide of carbon, chloroform, and benzene, but can be obtained in well formed crystals only from its solution in alcohol.

The crystals are fine very bulky plates with mother-of-pearl lustre. It melts at 56°, and boils at 256°—258° under a pressure of 751 mm. The specific gravity at 16° is 1·2656. The substance suffered no change when heated for several hours with a strong alcoholic solution of caustic potash to 220° in a sealed tube.

During the formation of β-chlornaphthalene in the way described above, a certain quantity of a liquid is always obtained which boils between 280°—300°; the author believes it to be a dichlornaphthalene.

β-chlornaphthalene may be obtained more easily in a pure state by rubbing up the sodium salt of the sulphoacid of β-naphthalene with an equivalent of phosphorus pentachloride, adding a second equivalent at the end of the reaction, and distilling over an open fire.

G. T. A.

## Action of Benzoyl Chloride on Dinitrophenol.

By M. Goldstein (Bull. Soc. Chim. [2], xxv, 394).

By the action of benzoyl chloride upon dinitrophenol, the author obtained a dibenzoyl derivative, crystallising in needles and melting at 201°. A solution of alcoholic potash splits it up into dinitrophenol and benzoic acid. When fuming nitric acid acts upon dinitrophenol the principal product is nitrobenzene.

C. A. B.

## Synthesis of Aromatic Ketones by Means of Carbonyl Chloride.

By W. Michler (Deut. Chem. Ges. Ber, ix, 716—718).

When dimethylaniline is saturated with carbonyl chloride, and after adding half a volume of dimethylaniline, the mixture is heated to 120°, a crystalline mass is obtained mixed with a blue colouring matter, which dyes the skin and wool. The product was boiled with water to remove free dimethylaniline, and the residue, after being washed, was treated with hydrochloric acid, which dissolved only a portion. On adding soda to the solution, a precipitate was obtained, which crystallised from alcohol in yellowish plates melting at 179°. This base is *tetramethyldiamidobenzophenone*, and its formation is easily explained, the author having previously shown, that by the action of phosgene on cold dimethylaniline, the chloride of dimethylamidobenzoic acid is formed:

$$C_6H_5N(CH_3)_2 + COCl_2 = C_6H_4\left\{\begin{matrix}COCl\\N(CH_3)_2\end{matrix}\right. + HCl.$$

By the further action of dimethylaniline on this chloride we have:

$$C_6H_4\left\{\begin{matrix}COCl\\N(CH_3)_2\end{matrix}\right. + C_6H_5N(CH_3)_2 = CO\left\{\begin{matrix}C_6H_4N(CH_3)_2\\C_6H_4N(CH_3)_2\end{matrix}\right. + HCl.$$

It forms with platinic chloride a double salt $CO[C_6H_4(NCH_3)_2]_2.2HCl + PtCl_4$ crystallising in golden-yellow plates.

The compound which is not soluble in alcohol consists of—

$C_6H_3N(CH_3)_2 \left\{ \begin{matrix} CO.C_6H_4N(CH_3)_2 \\ CO.C_6H_4N(CH_3)_2 \end{matrix} \right.$, and must be considered as a substitution-product of one of Zincke's dibenzoylbenzenes, and may be called *hexmethyltriamidodibenzoylbenzene.* It crystallises from alcohol in yellow transparent monoclinic plates, melting at 122°, and showing the faces $\infty P2$, $\infty P\infty$, P, $P\infty$ and 0P. Axes $a : b : c : = 0{\cdot}5865 : 1 : 0{\cdot}7138$.

C. S.

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**Anthrapurpurin and Flavopurpurin.** By E. SCHUNK and H. ROEMER (Deut. Chem. Ges. Ber., ix, 678—682).

ISOANTHRAFLAVIC acid yields anthrapurpurin (described by Perkin), and anthraflavic acid yields a new body, for which the authors propose the name of flavopurpurin. These purpurins are both obtained by the action of caustic potash. Their properties are as follows :—

| *Anthrapurpurin.* | *Flavopurpurin.* |
|---|---|
| Orange needles—anhydrous. | Golden-yellow needles, anhydrous. |
| Easily soluble in hot alcohol. | Easily soluble also in cold alcohol. |
| Scarcely soluble in boiling water. | The same. |
| The solution becomes red after long boiling. | The solution remains yellow on boiling. |
| Soluble with difficulty in ether. | The same. |
| Soluble in boiling acetic acid, crystallising on cooling in stellar groups of needles. | The same. |
| Soluble in concentrated sulphuric acid with violet-red colour. | Soluble, but with reddish-brown colour. |
| Soluble in caustic potash with violet colour. The shade is redder than that of an alcoholic solution of alizarin. | Soluble in caustic potash with purple colour, redder than anthrapurpurin : not so red as purpurin. On dilution or addition of a slightly dilute alkali, the solution appears pure red. The colour disappears after long standing. |
| Soluble with difficulty in hot baryta-water, with violet colour. | Only slightly soluble, with violet-red colour. |
| The solution shows absorption-bands. | The solution in thick layers shows bands. |
| Soluble in ammonia with violet colour. | Soluble in ammonia with yellowish-red colour. |
| The solution shows small bands. | No bands. |
| Soluble in sodium carbonate with violet colour. | Soluble in sodium carbonate with yellowish-red colour. |

| *Anthrapurpurin.* | *Flavopurpurin.* |
|---|---|
| Alcoholic solution of lead acetate gives a purple precipitate, which dissolves with a violet colour when boiled with lead acetate in excess. | Alcoholic solution of lead acetate gives a reddish-brown precipitate, only slightly soluble with red colour in excess. |
| Alcoholic solution of copper acetate gives a fine violet solution. | Alcoholic solution of copper acetate gives a red solution. |
| Slightly soluble in alum. | The same. |
| Melting point over 330°. | The same. |
| Sublimes in orange needles. | Sublimes in long needles resembling alizarin. |
| Dyes with mordants. | The same. |
| An alkaline solution gives two absorption-bands, which have the same position as those of alizarin. | An alkaline solution gives two bands, somewhat further from the red, and also a broad streak in the blue. |

According to Caro, isoanthraflavic and anthraflavic acid (dioxyanthraquinones) are derived from two different anthraquinone-disulphonic acids by the moderate action of alkalis: a stronger action produces anthrapurpurin (or flavopurpurin). The authors having received specimens of these two sulpho-acids agree with this view.

G. T. A.

**Anthraxanthic Acid.** By E. Ullrich and H. v. Perger (Deut. Chem. Ges. Ber., ix, 574—576).

The authors have studied the reactions of this compound, to compare them with its two isomerides, anthraflavic and isoanthraflavic acids, and give the following table:—

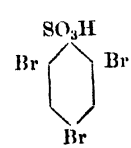
| Anthraflavic Acid. | Isoanthraflavic Acid. | Anthraxanthic Acid. |
|---|---|---|
| Crystallises from aqueous alcohol without water. | With water of crystallisation. | Without. |
| Less soluble in glacial acetic acid than in alcohol. | Same ..... | Same. Insoluble in cold acetic acid, sparingly soluble in the boiling acid. Sparingly soluble in cold, more freely in hot alcohol. |
| Crystallises from alcohol in needles. | In long, glistening needles. | Small glistening, golden-yellow needles. |
| Almost insoluble in benzene and ether. | Same ..... | Insoluble in benzene; more soluble in ether than in cold alcohol. |
| Dissolves in concentrated sulphuric acid with a yellow colour. | With a deep-red colour. | With a red colour. |

| Anthraflavic Acid. | Isoanthraflavic Acid. | Anthraxanthic Acid. |
|---|---|---|
| Insoluble in cold baryta-water. | Readily soluble.... | Almost insoluble; soluble in hot baryta-water; on cooling, the salt crystallises in reddish-brown needles. The ammoniacal solution of the acid is precipitated by baryta-water. |
| Sparingly soluble in cold lime-water, and still less in hot. | Readily soluble.... | Same as anthraflavic acid. |
| Soluble in an alcoholic solution of sugar of lead. | Same ..... | Very little soluble in the cold. |
| The barium-salt is decomposed by carbon dioxide; on boiling the salt is formed again. | Same ..... | Same. |
| Solution in alkalis yellowish-red. | Deep-red ..... | Yellowish-red. If the solution is not too diluted and contains an excess of alkali, the salt crystallises in orange-red needles. |
| Sublimes in needles or plates. | Same ..... | Heated in presence of air, a part is decomposed, and another sublimes in iridescent plates. |
| Does not fix on mordants.. | Same ..... | Same. |
| Yields alizarin on fusing with an alkali. | Yields a body having reddish-violet colour. | *Not changed.* |
| Contained in commercial alizarin. | Same ..... | Formed besides pure isopurpurin in the alizarin of Przibram and Co., and is formed only under certain conditions. |

C. S.

## Derivatives of Benzenesulphonic Acid. By H. LIMPRICHT (Deut. Chem. Ges. Ber., ix, 549—555).

1. *Tribromobenzenesulphuric Acid.*—Tribromobenzene prepared from tribromaniline can produce only a sulpho-acid having the following structure:—



Tribromobenzene heated with fuming sulphuric acid at 130°, yields on neutralisation and separation of the acid, an acid crystallising in fine, easily soluble needles, and forming the following salts:—

$C_6H_2Br_3SO_3K$ + aq. $(C_6H_2Br_3SO_3)_2Ba$ + 9 aq.

Chloride .... $C_6H_2Br_5SO_2Cl$, compact plates, m.p. 62°—63°.
Amide..... $C_6H_2Br_5SO_2NH_2$, microscopic needles.

Nitrotribromobenzenesulphonic acid is formed when the tribromo-acid is boiled with concentrated nitric acid, and crystallises in stellate groups of very soluble needles—

$C_6H(NO_2)Br_3SO_3K$ (anhydrous). $(C_6H(NO_2)Br_3SO_3)_2Ba + 1\frac{1}{2}$ aq.

2. *Metabenzenedisulphonic Acid.*—Meta- and para-benzenedisulphonic acids are formed simultaneously when excess of fuming sulphuric acid acts on benzene. If, however, the temperature be not raised too high, or continued for too long a time, the resulting mixture consists principally of the meta-acid, which is unattacked by nitric acid; but if sulphuric acid be also added, nitrobenzenedisulphonic acid is produced crystallising in colourless deliquescent needles. Its salts are all soluble:—

$C_6H_3(NO_2)(SO_3NH_4)_2$ (anhydrous).
$C_6H_3(NO_2)(SO_3K)_2$ ,,
$C_6H_3(NO_2)(SO_3Ag)_2$ ,,
$C_6H_3(NO_2)(SO_3)_2Ba$ + 4, 5 and 6 aq.
$C_6H_3(NO_2)(SO_3)_2Ca$ + 2 aq.
$C_6H_3(NO_2)(SO_3)_2Pb$ + 4 aq.

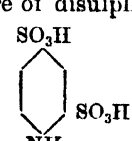
Chloride.. $C_6H_3(NO_2)(SO_2Cl)_2$. Flat prisms melting at 96°
Amide.... $C_6H_3(NO_2)(SO_2NH_2)_2$. Yellow needles melting at 242°.

When the nitro-acid is reduced by ammonium sulphide, amidobenzenedisulphonic acid is produced in prisms, easily soluble in alcohol and water, forming salts for the most part easy of solution:—

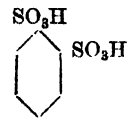
$C_6H_3(NH_2)(SO_3NH_4)_2$ + aq. $C_6H_3(NH_2)(SO_3)_2Ba + 3\frac{1}{2}$ aq.
$C_6H_3(NH_2)(SO_3Ag)_2$ $C_6H_3(NH_3)(SO_3)_2Pb$ + 4 aq.

The diazo-compound is formed when the solution of the amido-acid in absolute alcohol is treated with nitrous acid.

3. *Disulphanilic Acid.*—This acid, discovered by Buckton and Hofmann, does not appear to have been further studied until the present time; from it the diazo-compound may be obtained by treatment with nitrous acid dissolved in alcohol, and this when decomposed with absolute alcohol yields *benzene-metadisulphonic acid*, $C_6H_3(SO_3H)H(SO_3H)$. This was proved by converting the acid into the chloride, and thence into the amide, which when purified by crystallisation, melted at 229°, which is exactly the melting point of benzene-metadisulphamide. The structure of disulphanilic acid is, therefore—



4. *Metamidobenzenedisulphonic Acid, and another Benzenedisulphonic Acid.*—It appears probable that during the formation of metamidobenzenedisulphonic acid by the action of fuming sulphuric acid on metamidobenzenesulphonic acid, another isomeride is also formed: from the sulpho-acid the diazo-compound may be obtained, which, under the influence of alcohol and pressure, is converted into orthodisulphonic acid—

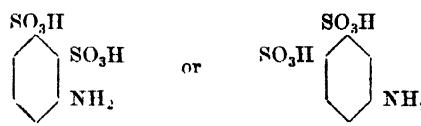



whose barium and potassium salts are very soluble and crystallise well.

Comparing the chlorides and amides of these three disulpho-acids, we find—

| | Ortho. | Meta. | Para. |
|---|---|---|---|
| Chloride..... | 105° | 63° | 132° |
| Amide ..... | 233° | 229° | 288° |

Meta-amidobenzenedisulphonic acid can, therefore, have only the formula—




5. *Dinitrobenzenesulphonic Acid.*—Instead of dinitrobenzenesulphonic acid being obtained when nitrobenzene was boiled with sulphuric acid and nitric acid, only the disulpho-acid was formed (*Ber.*, viii, 289); other methods were therefore resorted to. Dinitrobenzene (m.p. 89°) heated to 170° with fuming sulphuric acid, yields the monosulpho-acid, the barium salt of which crystallises in large, red, regular octohedrons; the same acid is obtained when meta-nitrobenzenesulphonic-acid is heated in a retort with an equal volume of fuming sulphuric acid and a double volume of nitric acid. The free acid has not yet been studied.

$$C_6H_3(NO_2)_2SO_3NH_4 \text{ (anhydrous?)}.$$
$$(C_6H_3(NO_2)_2SO_3)_2Pb + 3Aq.$$

Chloride .... $C_6H_3(NO_2)_2SO_2Cl$, small white crystals, m.p. 97°
Amide..... $C_6H_3(NO_2)_2SO_2NH_2$, short yellow needles, melting at 235°.

By ammonium sulphide it is converted into diamidobenzenesulphonic acid. By the treatment of the meta-nitrobenzenesulphonic acid with sulphuric and nitric acids another acid appears to be formed, whose barium salt is extremely soluble. From the analysis of the potassium salt it appears to be dinitrobenzenilic acid.

E. W. P.

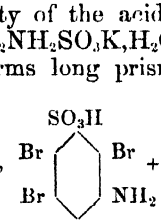
## Metamidobenzenesulphonic Acid and Bromobenzenesulphonic Acids. By H. BECKARTS (Liebig's Annalen, clxxxi, 209—231).

*Action of Bromine on Metamidobenzenesulphonic Acid.*—The products of this action when 2 or 3 molecules of bromine are employed are, as previously stated by Berndsen, di- and tri-brominated acids. With more than 3 mols. of bromine, *bromanil* is also formed, being the direct product of the action of bromine on the tribrominated acid.

*Action of Chlorine on Metamidobenzenesulphonic Acid.*—Chlorine in excess passed rapidly into a hot strong solution of the acid colours it red, brown, and finally yellow, and throws down crystals of *chloranil*, $C_6Cl_4O_2$. The same substance is produced by treating the acid with hydrochloric acid and potassium chlorate, whereby nearly the whole of the sulphur of the amido-acid is eliminated as sulphuric acid. The product of the action of 2 mols. only of chlorine on the amido-acid is *dichloramidobenzenesulphonic acid*, $C_6H_2Cl_2(NH_2)SO_3H,2H_2O$, which forms delicate white needles easily soluble in water.

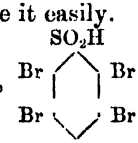
*Dibromometamidobenzenesulphonic acid*, $C_6H_2Br_2(NH_2)SO_3H$, is formed almost exclusively when the amido-acid is mixed with 2 mols. of bromine, and is also amongst the products formed by a larger proportion of bromine. It crystallises in anhydrous needles, which carbonise without melting when heated.

The author has determined the solubility of the acid and some of its salts at several temperatures. $C_6H_2Br_2NH_2SO_3K,H_2O$ forms pearly laminæ. $(C_6H_2Br_2NH_2SO_3)_2Ba,6H_2O$ forms long prisms, efflorescent in the air.

*Tribromometamidobenzenesulphonic acid*, 

$+H_2O$, is formed together with the preceding acid, from which it is separated by crystallisation. It forms delicate colourless needles, which dissolve easily in hot water and alcohol, and carbonise without melting when heated. The hot aqueous solution deposits bromanil on addition of bromine. $C_6HBr_3NH_2SO_3K.H_2O$ forms pearly laminæ easily soluble in hot water. $(C_6HBr_3NH_2SO_3)_2Ba.9H_2O$ forms small rhombic tables, which dissolve easily in hot water.

*Diazo-compound of Tribromometamidobenzenesulphonic acid*, $C_6H\left\{\begin{array}{l}Br_3\\N=N.\\SO_3\end{array}\right.$ Formed by passing a rapid current of nitrogen trioxide into a strong alcoholic solution of the acid. It forms small yellow rhombic tables which burn vividly when heated on platinum foil. It dissolves with red colour in hot water, nitrogen being evolved; and it is decomposed by boiling alcohol under pressure. Hydrobromic and hydriodic acids dissolve it easily.

*Tetrabromobenzenesulphonic acid*, 

$+5H_2O$, is formed by eva-

porating the foregoing diazo-compound with strong hydrobromic acid. It forms stellate groups of needles, which dissolve easily in water and alcohol and carbonise without melting when heated. $C_6HBr_4SO_3NH_4$ forms reddish laminæ. $C_6HBr_4SO_3K$ crystallises in needles. $(C_6HBr_4SO_3)_2Ba,1\frac{1}{2}H_2O$ forms delicate white laminæ. $(C_6HBrSO_3)Ca.8H_2O$ forms tufts of white needles. $(C_6HBr_4SO_3)_2Pb.4H_2O$ forms small prisms. $C_6HBr_4SO_3Ag.1\frac{1}{2}H_2O$(?) crystallises in small hexagonal prisms. The salts are all sparingly soluble in cold water. The *chloride*, $C_6HBr_4SO_2Cl$, formed by the action of phosphorus pentachloride on the acid, crystallises in reddish rhombic tables, which dissolve easily in ether, and melt at 91·5°. The *amide*, $C_6HBr_4SO_2NH_2$, dissolves easily in hot alcohol, from which it crystallises in microscopic needles. Its melting-point is above 250°.

*Nitrotetrabromobenzenesulphonic acid*, $C_6Br_4(NO_2)SO_3H.4H_2O$, is formed by the prolonged boiling of the tetrabrominated acid with strong nitric acid in a retort. It forms yellowish-white shining needles, which dissolve in hot water and alcohol, and carbonise without melting. Its potassium, ammonium, barium, calcium, lead and silver salts are all crystallisable and sparingly soluble in water. The *chloride*, $C_6Br_4(NO_2)SO_2Cl$, crystallises in white rhombic tables, which melt at 146°—147°. The *amide*, $C_6Br_4(NO_2)SO_2NH_2$, is a crystalline powder, dissolving sparingly in water, easily in alcohol. It melts to a dark liquid above 300°.

*Amidotetrabromobenzenesulphonic acid*, $C_6Br_4(NH_2)SO_3H.2H_2O$, formed by heating the nitro-acid with tin and hydrochloric acid, crystallises in microscopic needles, easily soluble in hot water and alcohol. Its aqueous solution, treated with bromine or chromic acid, yields no bromanil. The potassium, barium, and calcium salts are crystalline, and sparingly soluble in water.

*Diazo-compound of Amidotetrabromobenzenesulphonic acid*,

$$C\left\{\begin{array}{l} Br_4 \\ N{=}N. \\ SO_3 \end{array}\right.$$

Formed by passing a rapid current of nitrogen trioxide into an alcoholic solution of the amido-acid. It forms microscopic rhombic tables, which explode feebly when heated. It dissolves in hot water with decomposition, but is not decomposed by boiling with alcohol. Hot hydrobromic acid dissolves it with turbulent evolution of nitrogen, forming the following compound.

*Pentabromobenzenesulphonic acid*, $C_6Br_5SO_3H$, crystallises in fine laminæ and needles, which dissolve very sparingly in water. When heated to 180°—200° it evolves sulphur dioxide and yields a sublimate of white needles (probably pentabromobenzene), leaving charcoal. It is not affected by boiling with the strongest nitric acid or potash. $C_6Br_5SO_3NH_4$ crystallises from hot water in white laminæ. $C_6Br_5SO_3K,H_2O$ forms microscopic quadratic prisms. $(C_6Br_5SO_3)Ba,1\frac{1}{2}H_2O$ forms delicate laminæ. $(C_6Br_5SO_3)_2Ca.4H_2O$ forms white prisms. $C_6Br_5SO_2Ag,1\frac{1}{2}H_2O$ is a white crystalline powder. All the salts dissolve sparingly in cold water. The *chloride*, $C_6Br_5SO_2Cl$, crystallises in needles, which melt at 90°. The *amide*, $C_6Br_5SO_2NH_2$, is deposited from hot water as a crystalline powder, soluble in alcohol. It blackens without melting at 250°.

J. R.

**Orthobromobenzenesulphonic Acid.** By A. BAHLMANN (Liebig's Annalen, clxxxi, 203—208).

THE author prepares this acid by evaporating the diazo-compound of amidobenzenesulphonic acid with hydrobromic acid. To ensure a pure product, he converts the residue left on evaporation into potassium salt, treats this with phosphorus pentachloride, purifies the resulting chloride by crystallisation, and finally decomposes it with water at 140°—160°. The free acid, $C_6H_4BrSO_3H$, crystallises from concentrated solutions in long brownish deliquescent needles, which dissolve freely in alcohol. Its salts are all easily soluble in water.

$C_6H_4BrSO_3NH_4$ forms white tabular crystals. $C_6H_4BrSO_3K.H_2O$ crystallises in four-sided tables.

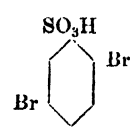
$(C_6H_4BrSO_3)_2Ba.xH_2O$ forms prisms or small needles with various proportions of water. $(C_6H_4BrSO_3)_2Ca.2H_2O$ forms small white tables. $(C_6H_4BrSO_3)_2Pb.3H_2O$ crystallises in transparent rhombic prisms. $C_6H_4BrSO_3.Ag$ forms white pearly laminæ, which decompose slowly in the light.

*Bromobenzenesulphonic chloride*, $C_6H_4BrSO_2Cl$, solidifies on standing in the cold. It crystallises from ether in tufts of pointed prisms, which melt at 51°.

*Bromobenzenesulphamide*, $C_6H_4BrSO_2NH_2$, forms long white brittle needles, which dissolve sparingly in water and melt at 186°.

*Dibromobenzenesulphonic Acid.*—On adding bromine-water to silver orthobromobenzenesulphonate so long as silver bromide is precipitated, a mixture of two isomeric dibrominated acids is formed, the potassium salts of which, when treated with phosphorus pentachloride, yield two *chlorides* separable by crystallisation:—

1. Transparent rhombic tables melting at 71° and yielding with ammonia an *amide* which crystallises in shining needles and melts at 192°. This chloride corresponds with the acid—




2. White needle-like crystals melting at 97°–98°, and yielding an *amide* which crystallises in dazzling-white silky needles very slightly soluble in cold water, and melting at 252°. The structure of the corresponding acid is unknown.

*Tribromobenzenesulphonic Acid.*—Bromine-water added in excess to silver orthobromobenzenesulphonate partly converts it into two tribrominated acids, which yield chlorides having the following characteristics:—

1. White needles melting at 56° and yielding a white pulverulent *amide* which melts at 202°.

2. Large rhombic tables melting at 72° and yielding an *amide* which melts at 187°.

The acid corresponding with the former of these chlorides is as yet unknown.

J. R.

## Action of Bromine on Orthamidobenzenesulphonic Acid.

By H. LIMPRICHT (Liebig's Annalen, clxxxi, 193—203).

WHEN this acid or its barium salt is gradually mixed with bromine (2 mols.), the products of the reaction are sulphuric acid or barium sulphate, tribromaniline, and monobromo- and dibromo-orthoamidobenzenesulphonic acids.

*Monobromorthamidobenzenesulphonic acid*, $C_6H_3Br(NH_2)SO_3H$, is formed in small quantity only. It crystallises in long needles, which dissolve easily in hot water, but very sparingly in cold water or alcohol. The *barium salt* forms white pearly laminæ, easily soluble in water. The free acid, suspended in alcohol, is converted by nitrous acid into small hexagonal tables of the *diazo-compound*, which explode when heated.

*Dibromorthamidobenzenesulphonic acid*, $C_6H_2Br_2(NH_2)SO_3H$, forms small rhombic anhydrous tables or large four-sided prisms containing 1 mol. of water. It is freely soluble in hot water and moderately in alcohol. The *potassium*, *sodium*, *barium*, and *lead salts* crystallise with water; the *calcium salt* is anhydrous: all dissolve in water. The potassium salt reacts with phosphorus pentachloride to form the sulphonic *chloride*, but on washing the product with water the acid is regenerated. The structure of the acid is represented by the following diagram (I): for when the acid is treated with bromine, that body replaces the group $SO_3H$, and tribromaniline (II) is produced:—

The *diazo-compound* of dibromorthamidobenzenesulphonic acid is obtained by passing nitrous acid into 95 p.c. alcohol in which the finely triturated acid is suspended. It forms microscopic prisms which burn vividly on platinum foil, evolve nitrogen when boiled with alcohol, dissolve in cold water and decompose instantly when heated therewith.

*Dibromobenzenesulphonic acid*, $C_6H_3Br_2SO_3H$.—The barium salt of this acid is obtained by boiling the foregoing diazo-compound with absolute alcohol, evaporating the alcohol, dissolving the residue in water, and precipitating with barium chloride. It crystallises from hot water in long yellow needles containing $3\frac{1}{2}$ mol. of water.

*Dibromobenzenesulphonic chloride*, $C_6H_3Br_2SO_2Cl$, forms large transparent crystals, which melt at 57·5°.

*Dibromobenzenesulphamide*, $C_6H_3Br_2SO_2NH_2$, is very sparingly soluble in hot water, and crystallises therefrom in very small needles, which melt at 203°.

*Nitrodibromobenzenesulphonic acid*, $C_6H_2Br_2(NO_2)SO_3H$, is formed by digesting the barium salt of dibromobenzenesulphonic acid with the strongest nitric acid. It gives on addition of barium chloride a precipitate of the barium salt, which crystallises from hot water in laminæ containing 2 mol. of water. The potassium salt reacts with

phosphorus pentachloride to form the *chloride*, $C_6H_2Br_2(NO_2)SO_2Cl$; which crystallises in small laminæ melting at 121°.

J. R.

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**On the Electrolysis of the Derivatives of Aniline, Phenol, Naphthylamine, and Anthraquinone.** By F. GOPPELSROEDER (Compt. rend., lxxxii, 1199—1201).

TOLUIDINE when electrolysed gives at the positive pole a brown substance which dissolves in alcohol, and dyes silk and wool brownish-yellow. Pseudotoluidine yields a violet colour, which changes to red on treatment with dilute nitric acid or potassium permanganate. A mixture of aniline, toluidine, and pseudotoluidine gives a red colour, and as secondary product a violet colour. From methyl-aniline a violet colour is formed. Diphenylamine yields a blue product which dissolves in alcohol. A mixture of diphenylamine with ditoluylamine and phenyltoluylamine gives a beautiful blue colour soluble in alcohol. Methyldiphenylamine also gives a blue or violet colour.

Phenol when electrolysed gives rise to a brown body at the positive pole; and salts of naphthylamine give naphthylamine violet.

The author has attempted to electrolyse anthraquinone, so as to obtain alizarin, but was long unsuccessful. The result was finally attained by the following process. Anthraquinone in very fine powder was placed in a very strong solution of caustic potash and a current passed; the potash was then heated till it fused. The mass assumes first a red and then a violet colour, owing to the formation of alizarate of potassium. This colour again rapidly changes to red and then to yellowish-brown, and if the heat be continued, it turns white. If the current be reversed when the last red colour has commenced, the mass becomes violet, then red, and yellow, owing to a reverse action, and this reversal admits of general application. These changes are usually due to the nascent oxygen, but in order to explain the processes which take place, the secondary products would have to be studied.

W. R.

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**On Chloronitranilines.** By F. BEILSTEIN and A. KURBATOW (Deut. Chem. Ges. Ber., ix, 633—635).

THE action of nitric acid on *p*-chloraniline results, as the authors have previously shown, in the formation of *o*-nitro- *p*-chloraniline, melting at 115°. This body, when treated with ethyl nitrite, yields *m*-chloronitrobenzene. The authors have now subjected *o*- and *m*-chloraniline to similar treatment.

The acetyl-compound of *o*-chloraniline, obtained by boiling that body with glacial acetic acid, crystallises in long broad needles melting at 87°—88°. When treated with a mixture of nitric and sulphuric acids, it yields the two following nitro-derivatives.

1. *m-Nitro-o-chloraniline* forms yellow needles easily soluble in alcohol and ether, and melting at 117°—118°. The acetyl-derivative, formed by heating the base with acetyl chloride, crystallises in colourless needles melting at 153°—154°. The base yields with alcohol and nitrous acid *p-chloronitrobenzene*: its constitution is, therefore, represented by the formula, $C_6H_3(\underset{1}{NH_2})\underset{2}{Cl}(\underset{5}{NO_2})$.

2. *p-Nitro-o-chloraniline* is contained in the mother-liquor of the foregoing compound. By treatment with nitrous ether it yields *m-chloronitrobenzene*, whence its constitutional formula is—

$$\underset{1}{C_6}(\underset{2}{NH_2})\underset{4}{Cl}H(NO_2)H_2.$$

*m*-chloraniline yields an acetyl-compound which forms large crystals melting at 72·5°. It also gives two nitro-derivatives, one only of which volatilises with water-vapour.

1. *o-Nitro-m-chloraniline* crystallises from carbon bisulphide in golden-yellow needles melting at 124°—125°: the acetyl-derivative melts at 115°. When treated with nitrous ether it yields *p*-chloronitrobenzene. Hence its formula is $\underset{1}{C_6}(\underset{3}{NH_2})HClHH(\underset{6}{NO_2})$, and that of the corresponding dichloronitrobenzene, $\underset{1}{C_6}\underset{3}{Cl}HClH_2H(\underset{6}{NO_2})$. The latter body melts at 33°, and yields by reduction a chlorophenylenediamine melting at 72°. It is violently acted on by alcoholic potash, the product being a crystalline substance melting at 62°—63°.

2. Non-volatile *p-nitro-m-chloraniline* crystallises from benzene in yellow laminæ which melt at 156°—157°: the acetyl-derivative melts at 141°—142°. By the action of nitrous ether it yields *o-chloronitrobenzene*, melting at 32·5° and boiling at 243°. The constitutional formula of *p*-nitro-*m*-chloraniline is, therefore $\underset{1}{C_6}(\underset{3}{NH_2})H\underset{4}{Cl}(NO_2)H_2$.

J. R.

## Derivatives of Benzanilide and other Compounds.

By H. Hübner (Deut. Chem. Ges. Ber., ix, 774—779).

1. *Metanitrobenzanilide.*—This body is formed, together with ortho- and para-nitrobenzanilide, by the action of nitric acid on benzanilide. It is isolated by exhausting the crude product with cold chloroform, which dissolves the ortho- and meta-derivatives, evaporating the solution, and treating the residue with boiling alcohol, which, as it cools, deposits first the meta-compound in yellow needles. After recrystallisation it melts at 144°. It is insoluble in water. With soda-ley it yields metanitraniline, melting at 108°.

2. *Orthonitracetanilide.*—When acetanilide is treated with nitric acid, and the liquid is diluted with water, paranitracetanilide alone is deposited, the ortho-compound remaining in solution. The latter is taken up from the acid liquid by chloroform, and when crystallised from alcohol or water forms yellow laminæ melting at 78°. Heated to 140° with strong hydrochloric acid, it yields orthonitraniline melting at 71°.

3. *Metamidobenzanilide*, $C_6H_4.NH_2.(NH.COC_6H_5)$.—Obtained from the nitro-compound described above. It forms colourless rhombic prisms which are nearly insoluble in chloroform. The hydrochloride, sulphate, and nitrate all crystallise in long needles soluble in water.

4. *Anhydrobenzoyldiamidobenzene.*—Previous researches on this substance showed that it contains the group NH, and the author has now succeeded in replacing the hydrogen of that group by amyl and ethyl,

by heating the substance with excess of amyl or ethyl iodide in sealed tubes. The *amyl* compound, $C_6H_4NC.C_6H_5.NC_5H_{11}$, crystallises in small rhombic tables, which melt at 270°. It forms crystallisable salts, soluble in water. The *ethyl* compound, $C_6H_4.NC.NC_2H_5$, likewise forms salts easily soluble in water. The formation of both these compounds is accompanied by that of another body which is not yet investigated.

5. *Action of Cyanogen Iodide on Amides.*—Orthodiamidobenzene and cyanogen iodide when triturated together react in the manner indicated by the equation—

$$2C_6H_4(NH_2)_2 + CNI = NH_4I + C_{13}H_{12}N_4.$$

The last product is a base easily soluble in alcohol, forming a solution which on addition of water deposits needles of the colour of precipitated gold. It sublimes in red needles, which dissolve in acids, and are reprecipitated of a golden yellow colour by alkalis. It gives with sulphuric acid a deep blue solution, which yields dark blue octohedral crystals of the salt $C_{13}H_{12}N_4.H_2SO_4 + 2\frac{1}{2}H_2O$. The base forms crystallisable salts also with hydrochloric and nitric acids. Heated to 150° with excess of benzoyl chloride, it yields the compound $C_{13}H_{11}N_4.C_6H_5CO$, which crystallises in small yellow needles.

Paradiamidobenzene and cyanogen iodide similarly react to form a base crystallising in yellow needles.

J. R.

## On Aniline-black.

By R. Nietzki (Deut. Chem. Ges. Ber., ix, 616—620).

The aniline-black examined by the author was prepared by Müller's process, which consists in heating an aqueous solution of aniline hydrochloride, potassium chlorate, copper sulphate, and ammonium chloride. The product was purified by dissolving it in aniline, precipitating with hydrochloric acid, and boiling the dried precipitate with alcohol and dilute hydrochloric acid. It gave on analysis numbers agreeing approximately with the formula $C_{18}H_{15}N_3.HCl$. Assuming this to be its true composition, aniline-black may be regarded as the hydrochloride of a base formed as follows:—

$$3C_6H_5H_2N = \left.\begin{matrix} C_6H_4H \\ C_6H_4H \\ C_6H_4H \end{matrix}\right\} N_3 + 6H.$$

A body thus constituted must contain three replaceable atoms of hydrogen. Attempts to introduce ethyl or methyl into aniline-black have hitherto failed, but on boiling the free base with aniline, it undergoes a remarkable alteration, and afterwards gives up to alcohol a bluish-purple substance, the hydrochloride of a new base, which is still under investigation.

Aniline-black heated on the water-bath with fuming sulphuric acid, is converted into a sulphonic acid, which dissolves with dark-green colour in water, and forms with alkalis ink-like solutions, from which

acids precipitate it in greenish-black flocks. The salts of this acid have not been obtained in the crystalline state.

J. R.

## The Theory of the Formation of Aniline-black.

By A. ROSENSTIEHL (Bull. Soc. Chem. [2], xxv, 356—365).

IT has been observed that three substances are essentially necessary in the formation of aniline-black, viz., the presence of aniline salts, chlorates, and metallic salts (copper salts having the preference). It was believed formerly that copper salts acted in the following manner. A cupric salt was first in contact with the aniline salt, then immediately became reduced to cuprous salt, thus allowing the liberated oxygen to act upon the dye. This theory is incorrect, as there is no reduction of the cupric salt to cuprous. The author formerly considered the presence of a small quantity of copper indispensable to the formation of aniline-black. The copper, however, is only intermediary in bringing the oxidising agents to act upon the cloth, a fact which was proved by the author as follows. A piece of cloth was impregnated with an aniline salt, and suspended in a vessel containing a little ozone or chlorine, when a black colour was rapidly produced. Copper chlorate is a very unstable salt, is easily destroyed in the presence of tissue at 35° C., and decomposes (giving off chlorine and its lower oxides as a yellow gas) when heated in a flask to 60°, a basic salt remaining behind. It acts rapidly upon hydrochloride of aniline, the action resulting in the formation of a black. In order to ascertain whether the gaseous products arising from the decomposition of metallic chlorates really favoured the formation of aniline-black, the author made the following experiments. Four flasks were taken. No. 1 contained a few grams of ammonium chlorate (which is the most unstable alkaline salt); No. 2 contained a mixture of this salt with a little cupric sulphate; No. 3, copper chlorate; No. 4, a mixture of copper chlorate and a vanadium salt. No reaction took place in the cold, but on applying heat by means of a water-bath, it was observed that aniline-black was first produced in flask No. 4, then in Nos. 2 and 3, whilst No. 1 remained unchanged. Thus it appears highly probable that the colour is developed by the action of gaseous products arising from the decomposition of metallic chlorates. Further experiments were made with a few cubic centimeters of aqueous solutions of chlorine, hypochlorous acid, chlorous acid, and chlorine tetroxide placed at the bottom of different flasks, and in each of them (above the solutions) was suspended a piece of cloth impregnated with an aniline salt. The action was rapid, for the black developed as the gases diffused in the flasks, the cloth first becoming green, then blue-black. This effect was produced in eight minutes, but if the cloth was exposed to the action of gases for a longer time the colour became rose. From the above it is quite evident that aniline-black can be produced by the action of gaseous bodies, such as the above mentioned, at the ordinary temperature without contact with any metal. The best black is obtained by the action of chlorous acid and chlorine tetroxide, as it is found that chlorine and hypochlorous acid act too energetically (the black appear-

ing spotted with red or violet), and their action cannot be regulated without great difficulty. The green substance formed at first becomes black by the gradual action of the chlorine oxides, but its formation is much accelerated if the cloth be immersed in dilute solutions of these gases. This green is called "emeraldine." Zürcher expresses the following opinion regarding the composition of aniline-black. "As first formed, aniline-blacks possess a dark greenish-blue colour, the colour of a mixture of emeraldine and aniline-black; the pure black is obtained only in the alkali-bath." Brandt first observed the simultaneous occurrence of the two blacks in 1872. He found one of them to be very solid, scarcely acted upon by any chemical reagents, and considered it a chlorinated aniline derivative; the other, which results from the oxidation of aniline salts, is not so solid as the first, and becomes green in the presence of the least acidity. Both resist the action of soap perfectly. Brandt further considers the presence of both necessary for the formation of a perfect black. Rosenstiehl comes to the following conclusions:—

1st. Aniline-black is produced at the ordinary temperature when an aniline salt is exposed to the action of a hydrogen-abstracting medium, such as nascent oxygen, chlorine, and its lower oxides.

2nd. Mixtures of chlorates with metallic salts give rise to the formation of the above-mentioned oxides of chlorine, and hence the gradual production of aniline-black, owing to the ease with which metallic chlorates are decomposed.

C. A. B.

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**Compounds of Sulphocyanic Acid with the more important Cinchona Alkaloïds.** By O. HESSE (Liebig's Annalen, clxxxi, 48).

WHEN a moderately concentrated warm aqueous solution of quinine hydrochloride is mixed with potassium sulphocyanate, and the whole cooled, the turbid liquid deposits white needles having the composition $C_{20}H_{24}N_2O_2.HCNS + H_2O$; dissolved in chloroform mixture this gives the rotatory power—

$$(\alpha)_D = -129{\cdot}31.$$

The salt dissolves at 20° in 562 parts of water, and is readily soluble in hot water and in alcohol, but only to a very minute extent in ether. Its aqueous solution forms with phenol a crystalline precipitate, consisting of a compound of phenol with quinine sulphocyanate.

If dilute sulphuric acid, potassium sulphocyanate, and quinine hydrosulphocyanate are brought together, sulphur-yellow needles of the acid salt $C_{20}H_{24}N_2O_2.2HNCS.\frac{1}{2}H_2O$ separate.

In the same way cinchonidine forms an oily acid hydrosulphocyanate and a crystalline neutral salt, which when air-dry is represented by the formula $C_{20}H_{24}N_2O.HCNS$. This dissolves at 20° in 305 parts of water, and behaves with hot water, alcohol, ether, and phenol like the quinine salt. Similarly quinidine (the so-called "conchinine" of the author) forms an anhydrous neutral salt, $C_{20}H_{24}N_2O_2.HCNS$, soluble at 20° in 1,477 parts of water, and difficultly soluble in boiling water, and only sparingly soluble in boiling alcohol; also an acid salt,

$C_{20}H_{24}N_2O_2.2HCNS.H_2O$, crystallising in long sulphur-yellow prisms; whilst cinchonine forms a crystallisable sulphocyanate, $C_{20}H_{24}N_2O.HCNS$, soluble in 474 parts of water at 20°, and readily soluble in boiling water and in alcohol.

Although the crystalline characters of these various sulphocyanates are different, it does not seem practicable to make use of their differences as a means of detecting qualitatively an admixture of one with the other, inasmuch as substances of known purity occasionally give rise to crystalline crops, which when examined under the microscope simulate exactly the appearances of the substances obtained from various mixtures of the alkaloïds.

C. R. A. W.

**Phenol Compounds of the Cinchona Alkaloïds.** By O. HESSE (Liebig's Annalen, clxxxi, 53).

THE author and Jöbst have already shown (*Liebig's Annalen*, clxxx, 248) that phenol gives crystallisable compounds with quinine hydrochloride, hydrobromide, and sulphate; similarly, when an aqueous solution of phenol (1 to 25) is added to a hot solution of neutral cinchonidine sulphate, there crystallises out on cooling a body containing the elements of the two substances, and expressed by the formula $2C_{20}H_{24}N_2O.SO_3.C_6H_6O.5H_2O$, the water of crystallisation being lost at 110°. These crystals dissolve in 425 parts of water at 15°, readily in boiling water; they are crystallisable from hot alcohol, and are precipitated from an aqueous solution almost completely by phenol water. With ferric chloride this compound gives only a slight dark yellow tint, whence the phenolic hydroxyl would appear to be functionally altered, since the characteristic tint is no longer developed. Addition of dilute acids, however, causes the separation of phenol, whilst alkaloids also set phenol free from the compound, simultaneously precipitating the base. The caustic action of phenol is not exhibited by the compound.

Similarly with cinchonidine hydrochloride an analogous body is formed, represented by the formula $C_{20}H_{24}N_2O.HCl.C_6H_6O.H_2O$, after drying in an exsiccator. At 100° it loses not only water of crystallisation, but also phenol. In chloroform it dissolves readily, in ether only very sparingly; in water at 15° it dissolves to the extent of 1 part in 46. In 97 per cent. alcohol at 15° it gives the rotatory power—

$$(\alpha)_D = -\ 83{\cdot}75$$

whence for the alkaloïd

$$(\alpha)_D = -\ 124{\cdot}12$$

With ferric chloride this compound behaves as the sulphuric derivative; the phenol possesses in it no caustic power; on the other hand, acids readily regenerate phenol from it.

In order to gain some insight into the constitution of this body, the chlorinated derivative was dissolved in phenol water and platinic chloride added; the resulting salt, however, was only cinchonidine platinochloride. Equivalent quantities of phenol and cinchonidine

were dissolved in hot dilute alcohol; on cooling, an oil separated which became crystalline on standing; this appeared to be veritably a compound of phenol and cinchonidine, as it regenerated phenol on addition of acids. It did not, however, give any violet colour reaction with ferric chloride, whence the author concludes that the added phenol in these compounds is situated in the alkaloïdal part of the molecule.

Quinidine (the conchinine of the author) and cinchonine salts give compounds with phenol water, but these are oily amorphous bodies. They are precipitated from aqueous solution by further addition of phenol water. Quinicine and cinchonicine sulphates give analogous compounds much less perfectly precipitated by excess of phenol water. Quinamine sulphate, however, gives no precipitate with phenol water.

Cinchona alkaloïds, especially cinchonidine, may thus be used as a test for phenol, or conversely phenol can be employed as a reagent for certain of these alkaloïds.

C. R. A. W.

*Note by Abstractor.*—The mode of formation and general properties of the substances above described, and especially the action on them of acids, alkalis, and platinic chloride, seem to indicate that these bodies are really double salts, in which the polyacid alkaloïd is united with two different acids, of which phenol is one; these bodies may be compared with ethylene aceto-butyrate, $C_2H_4\left\{\begin{matrix}C_2H_3O_2\\C_4H_7O_2\end{matrix}\right.$, or with strontium aceto-nitrate, $Sr\left\{\begin{matrix}NO_3\\C_2H_3O_2\end{matrix}\right.$, and analogous derivatives of polyacid metals. These substances, and the similar bodies obtained by Jöbst and Hesse from quinine, may be thus compared with other cinchona-alkaloïd salts.

| | | |
|---|---|---|
| MONO-ACID. | Cinchonine monohydrochloride.. | $C_{20}H_{24}N_2O,HCl$ |
| „ | Quinine monosulphate ("neutral" sulphate) ..... | $(C_{20}H_{24}N_2O_2)_2,H_2SO_4$ |
| „ | Cinchonidine phenolate ? ..... | $C_{20}H_{24}N_2O,C_6H_6O$ ? |
| SESQUI-ACID. | Cinchonidine phenolo-sulphate.. | $(C_{20}H_{24}N_2O)_2\left\{\begin{matrix}C_6H_6O\\H_2SO_4\end{matrix}\right.$ |
| „ | Quinine phenolo-hydrochloride.. | $(C_{20}H_{24}N_2O_2)_2\left\{\begin{matrix}C_6H_6O\\HCl\\HCl\end{matrix}\right.$ |
| „ | Quinine phenolo-sulphate ..... | $(C_{20}H_{24}N_2O_2)_2\left\{\begin{matrix}C_6H_6O\\H_2SO_4\end{matrix}\right.$ |
| DI-ACID. | Quinidine dihydrochloride ..... | $C_{20}H_{24}N_2O_2,2HCl$ |
| „ | Quinine disulphate ("acid" sulphate)..... | $C_{20}H_{24}N_2O_2,H_2SO_4$ |
| „ | Cinchonidine phenolo-hydrochloride | $C_{20}H_{24}N_2O\left\{\begin{matrix}C_6H_6O\\HCl\end{matrix}\right.$ |

C. R. A. W.

## Aricine and Allied Substances. By O. HESSE (Liebig's Annalen, clxxxi, 58).

THE author reviews the experiments made by Pelletier and Coriol in 1829 on a bark of doubtful cinchona nature, from which these chemists obtained a base crystallising in white transparent crystals soluble in alcohol and ether, insoluble in water, and capable of forming an acid and a neutral sulphate; by Leverköhn, who obtained from false calisaya bark (cinchona from Cusco) a gelatinous apparently non-crystalline sulphate of a base termed by Buchner *cusconine*; by Manzini, who extracted from pale tenchina bark an alkaloïd which he called *cinchovatine*, but which the author subsequently found to contain also cinchonine, and which was subsequently found by H. Bourchardat and Winckler to be identical with aricine; and by David Howard, whose results the author considers to be due to his having obtained an impure *paricine* (containing cinchonine ?).

The alkaloïds of a Cusco bark obtained from De Vrij were extracted by the author in the ordinary way; the concentrated neutral sulphuric acid solution yielded crystals of cinchonidine sulphate, and then gelatinised to a mass of microscopic prisms of the same containing a little quinine sulphate; the filtrate from these contained cinchonine and amorphous bases from which nothing characteristic could be isolated. Other samples of Cusco bark yielded only cinchonine and traces of amorphous bases; the author considers De Vrij's bark not to have been genuine Cusco bark. Another Cusco bark (*China de Cusco vera* of Wiggers) identical with that employed by Pelletier and Coriol yielded cinchonine, a little cinchonidine, and amorphous bases, but no other crystallisable alkaloïd.

Commercial "pale tenchina" bark carefully examined and selected by Wiggers yields no cinchovatine or aricine, but only cinchonine and traces of quinidine (the conchinine of the author), and amorphous bases. Other pale tenchina barks from France yielded cinchonidine also; but this bark appeared to contain an admixture of other varieties, although specimens could be readily picked out agreeing in all respects with the sample obtained from Wiggers.

Cinchovatine prepared by Winckler and examined by the author gave no blue fluorescence when dissolved in sulphuric acid; it formed fine white prisms which gave numbers agreeing with those required for cinchonidine; it melted at 208° (not corrected) and gave the rotation $(\alpha)_D = -107{\cdot}25$, whilst pure cinchonidine melts at 205° (not corrected) and gives the rotation $(\alpha)_D = 106{\cdot}89$ under the same conditions. It gave a hydrochloride indicated by $C_{20}H_{24}N_2O.HCl.H_2O$, a platinum salt $C_{20}H_{24}N_2O.2HCl.PtCl_4$, a sulphate $(C_{20}H_{24}N_2O)_2H_2SO_4$ anhydrous after drying in the air, and giving the rotation $(\alpha)_D = -172{\cdot}20$, whilst pure cinchonidine sulphate gave $(\alpha)_D = -172{\cdot}37$, and finally the hydrochloride and the sulphate gave with phenol water compounds precisely resembling those obtained with cinchonidine.

Aricine sulphate of commerce consisted mainly of a sulphate forming on recrystallisation a gelatinous mass of minute needles, together with some cinchonine and quinine sulphates and a trace of resinous matter insoluble in water. The base in these small crystals gave on analysis

numbers agreeing with cinchonidine; it melted at 205°, and gave the rotation $(\alpha)_D = -107{\cdot}25$; the sulphate crystallised from a large bulk of water, formed crystals containing $(C_{20}H_{24}N_2O)_2H_2SO_4.3H_2O$; with phenol water and Seignette salt it formed difficultly soluble compounds precisely agreeing in all respects with those from cinchonidine.

Hence the author concludes that the bodies described as aricine and cinchovatine are simply more or less pure cinchonidine, as is also a lævo-rotatory crystalline base extracted in 1873 by De Vrij from Jamaica bark.

C. R. A. W.

## On the Relation of Acid Albumin to Alkali Albuminate.

By Isidor Soyka (Pflüger's Archiv. für Physiologie, xii, 347—377).

The author's experiments on acid albumin (obtained from egg albumin and serum albumin) and on syntonin, show that, for the precipitation of acid albumin from an alkaline solution in presence of neutral phosphates, the addition of more acid is required than without the presence of the phosphate; that, therefore, the precipitation is retarded by the neutral phosphate, and occurs only when there is a certain excess of acid, in other words when the neutral phosphate has, in part at least, become converted into acid phosphate. The author, repeating the experiments of Soxhlet on alkali albuminate free from salt, prepared from egg albumin according to Lieberkühn's method, lays down the following rule:—The alkaline solution of this albuminate is not precipitated in presence of phosphates on the addition of an acid, as long as the proportion of acid to neutral phosphate does not exceed that of nine molecules to one molecule. Experimenting further, the author found, in order that acid albumin in an alkaline solution in presence of neutral alkali phosphate may be held in solution after the addition of acid, it is necessary that the relation should be such that the acid phosphate which is formed does not exceed nine times that of the neutral phosphate by molecule; if this occurs precipitation sets in. He finds, in short, that acid albumin in an alkaline solution in presence of neutral phosphate behaves in regard to acids in precisely the same manner as albuminate. If an alkaline solution of acid albumin or albuminate, with or without neutral phosphate, which has been treated with just sufficient acid to redissolve the albuminous body, is boiled, a flocculent precipitate occurs, whereas solutions which contain more acid remain clear on boiling. Acid albumin, the author concludes, differs in no wise from alkali albuminate in regard to its reactions.

For the body, which combined with an acid forms acid albumin, and in combination with a base forms a compound called albuminate, the author proposes the name of *proteïn*. Acid albumin would then be called *acid proteïn* (*e.g.*, hydrochloride or acetate of proteïn), and what is now known as albuminate would become *metallic proteïn* (*e.g.*, soda proteïn, potash proteïn). The difference which occurs in the form of the precipitate in these bodies does not, according to the author, depend upon whether it is acid albumin that is precipitated from an acid solution, or alkali albuminate from an alkaline one, but upon the *origin of*

*these substances.* Noticeable and constant differences are observed for example between the albuminate from albumin and that from meat, and between syntonin and acid albumin derived from albumin. The precipitates from egg albumin are always milk-white, flocculent and settle into a small volume; whereas those from meat are transparent, and gelatinous.

In conclusion the author says:—The acid albumins and albuminates belong to one and the same albuminous group; they differ only in so far that they both contain the same substance, proteïn, united in the one case to acids, in the other to bases. The soluble albuminous bodies are, therefore, to be divided into three groups only, albumin, proteïn, and globulin.

E. C. B.

**On the Optical and Chemical behaviour of certain Albuminous Substances, especially Dialysed Albumin.** By HERMANN HAAS (Pflüger's Archiv. für Physiologie, xii, 378—410).

THE author having doubts as to the trustworthiness of the polarisation test for the quantitative estimation of albumin in urine, and especially with regard to the influence of chloride of sodium on the specific rotation of albumin, was led to subject the behaviour of albumin in this respect to a systematic examination. The instrument employed was Wild's polaristrobometer. The author finds that on dilution of a natural solution of albumin with water, *i.e.*, a simultaneous diminution of the content of salt and albumin, the specific rotation of the albumin is not changed. The weighed quantities of albumin correspond with those calculated from the rotation, in a solution containing from ·08 to 3·95 per cent. of albumin. This corroborates Hoppe's experiments. The author next shows that, on dilution of a natural solution of albumin with a dibasic or monobasic phosphate, the rotation of the albumin does not change in any noticeable degree. In opposition to Aronstein, the author was unable, even after dialysis extending over several weeks, and by using large quantities of distilled water, to obtain albumin quite free from salt. The dried substance contained on an average one per cent. of ash. From an examination of five portions of dialysed egg albumin (from which the precipitable forms of albumin, globulin, and albuminate had been removed by various methods, and also the extractive matters soluble in alcohol and ether), the author estimates the coëfficient of rotation of egg albumin to be 38·1°. The separate observations varied between ·5° below and 1·0° above this average. The concentration, he finds, is without influence on the specific rotation of egg albumin. From further experiments the author concludes with certainty that the salts contained in natural solutions of albumin, no matter in what quantity present, do not exert the least influence on the coëfficient of rotation. He notes especially that carbonate of soda does not exert an immediate influence on the rotation. The author explains some experiments in which he found that the addition of sodium chloride to the albuminous urine increased the rotation, by supposing that the fluid contained, in addition to soluble albumin,

suspended albumin (globulin), which became dissolved only after the addition of the salt. The author also experimented with the polaristrobometer on serum albumin, globulin, and alkali albuminate.

E. C. B.

## Physiological Chemistry.

**On the Proof of the presence of Carbamic Acid in Animal Fluids.** By FRANZ HOFMEISTER (Plüger's Archiv. für Physiologie, xii, 337—347).

THIS paper is based on one by E. Drechsel, in which he attempts to prove that in the animal organism urea is formed from "carbamic acid," and that carbamic acid is formed directly from glycocine. He also obtained the reactions for carbamic acid in the blood-serum of dog. These reactions, which depend on the easy splitting of carbamic acid into carbonic acid and ammonia, are of value, according to the author, provided that these bodies cannot be due to any other substances present at the same time. The author considers Drechsel's experiments at length, and shows that the methods employed in them are untrustworthy. He finally concludes, "that the formation of carbamic acid by the oxidation of amidic acids, as well as the presence of the same in the blood, cannot be considered as proven."

E. C. B.

**Influence of Carbonic Acid on the Respiration of Animals.** By F. M. RAOULT (Compt. rend., lxxxii, 1101).

SLOW chemical actions are generally impeded by the presence of the products formed; the author believes that the oxidation of the blood is retarded by the presence of the carbonic acid formed. In experimenting on rabbits, he found that for every hundred litres of air inhaled, containing 20·8 litres of oxygen and no carbonic acid, 2·3 litres of carbonic acid are formed, and 2·8 litres of oxygen consumed, while if the same volume of gas is taken, containing 20·8 litres of oxygen and 12·1 litres of carbonic acid, only 0·9 litre of carbonic acid is produced, and 1·1 litre of oxygen is consumed.

But an animal breathing impure air inhales 97 litres of air an hour, instead of the normal quantity, 71 litres, and thus corrects the noxious effects of carbonic acid to some extent. Nevertheless, after necessary correction had been made, it was found that the presence of carbonic acid in inhaled air is an obstacle to hematose.

W. R.

**On the Existence in the Animal Organism of a New Substance exhibiting the Absorption-spectrum of Blood.** By H. STRUVE (Deut. Chem. Ges. Ber., ix, 623—627).

THE author has obtained from beef and veal a substance exhibiting an absorption-spectrum which exactly coincides with that of hæmoglobin,

but unlike the latter, is not affected by alkaline sulphides or acids. This substance occurs also in considerable quantity in the liver of the calf and the ox, and in traces in human liver. It is extracted by ether. Preliminary experiments seem to show that it is a compound of an acid and a base. The subject is being further investigated.

J. R.

### The Chemistry of Diabetes Mellitus.

By C. T. KINGZETT (Chem. News, xxxiii, 183).

THE author theoretically criticises the views of Dr. Pavy with regard to the production of glycosuria by the effect of oxygenated blood upon the liver (*Proc. Roy. Soc.*, vols. xxiii—xxiv). He considers that a ferment produced by oxygen could not be similar to that produced by carbonic oxide, and consequently the production of glycosuria would be brought about in a different way in each instance.

F. J. L.

### Decomposition of Sodium Salicylate in the Organism.

By BINZ (N. Rep. Pharm., xxv, 205—210).

THE author mentions that in a debate on the use of salicylic acid and sodium salicylate, it was omitted to discuss the question whether it was admissible to consider sodium salicylate as being chemically inactive in the organism.

Since the blood-vessels always produce carbonic acid, and the blood, in spite of its alkalescency, contains large quantities of this gas, in a free or continually dissociating state, which gas has the property of liberating the acid from sodium salicylate, the author thinks it improbable to suppose that this salt, which is decomposed by $CO_2$, would pass as such through an organism containing large quantities of nascent carbonic acid. The author further mentions that all tissues undergoing any energetic changes produce carbonic gas, and that at such places a similar decomposition of the salt will be the result. The behaviour of the organism to pyrogallic acid affords further proof to the fact of the former not being simply an alkaline mixture.

D. B.

## Chemistry of Vegetable Physiology and Agriculture.

### On the Interchange of Ammonia between Air and Arable Land.

By TH. SCHLOESING (Compt. rend., lxxxii, 1105—1108).

IT is usually believed that soil absorbs ammonia with rain and dew, and parts with it in drying, and many think that this is the source of the ammonia in the air; but the amount of loss and gain is unknown.

The author, in order to decide this point, passed pure air over three

hectolitres of soil placed in a trough; the air, after passing over the earth contained less ammonia than ordinary air, so that the soil, if it had been exposed to ordinary air, would have absorbed ammonia.

Soil was exposed to air for some weeks, and on analysis, gave the following results :—

| Earth from Boulogne. | $NH_3$ in 50 grams. Mgr. | Earth from Neauphlé-le-château. Not calcareous. | $NH_3$ in 50 grams. Mgr. |
|---|---|---|---|
| 30th July, 1875 .... | 0·797 | 1st August, 1875.... | 0·219 |
| 6th Aug., „ .... | 0·996 | 9th „ „ .... | 0·964 |
| 13th „ „ .... | 1·044 | 16th „ „ .... | 1·871 |
| 20th „ „ .... | 1·626 | 23rd „ „ .... | 2·221 |
| 27th „ „ .... | 1·730 | 30th „ „ .... | 2·391 |
| 3rd Sept., „ .... | 1·694 | 6th Sept., „ .... | 3·011 |
| 10th „ „ .... | 2·094 | 13th „ „ .... | 3·591 |
| 17th „ „ .... | 2·504 | 20th „ „ .... | 4·141 |

The ammonia therefore is not evolved during the drying of the earth, but is absorbed.

Moist earth transforms ammonia into nitrates, so that it is constantly being removed from the soil, which retains its capacity of absorbing more, according to the rapidity of the nitrification.

From the 19th June to the 4th July (14 days) 50 grms. of soil, kept moist by watering, contained 0·775 mgrms. of ammonia and converted 4·175 mgrms. into nitric acid, while the same soil under cover, contained 0·73 mgrms., and converted 1·630 mgrms. into nitric acid. The difference is 2·59 mgrms. in favour of the exposed soil. In 28 days, from another experiment, 50 grms. absorbed 4·097 mgrms. of ammonia more when exposed than when covered: 1 hectare of soil would therefore absorb in 14 days 2·59 kilos. of ammonia, and in one year 63 kilos.

This shows conclusively that soil absorbs ammonia from the air, to convert it into nitric acid.

W. R.

## The Assimilation of Atmospheric Nitrogen by Soil.

By Th. Schloesing (Compt. rend., lxxxii, 1202—1209).

The author previously stated his belief that the nitrogen of the air is oxidised by electricity, and that the nitric acid on reaching the earth is carried out to the sea-shore, changed into ammonia, and again restored to the air along with aqueous vapour. Dehérain stated lately that earth can assimilate nitrogen without having it presented as nitric or nitrous acid or ammonia. Boussingault showed that soil does not absorb nitrogen, even when kept in air for 10 years, but Dehérain has cited numerous experiments to prove that, under the influence of vegetation, nitrogen is assimilated. In repeating Dehérain's experiments of heating glucose, soda, and nitrogen in sealed tubes, the author never found less nitrogen present at the end of the operation

than at the beginning. Dehérain concluded that the nitrogen liberated as ammonia by subsequent combustion of the glucose with soda-lime, arose from the absorbed nitrogen; this nitrogen was probably owing to the nitrates in the soda-lime reduced by the glucose. Nor when the nitrogen was left in contact with new earth, were positive results obtained, for in every case the nitrogen remained constant or slightly increased.

W. R.

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## Evolution of Oxygen from Plants under Boiled Water.

By J. Böhm (Deut. Chem. Ges. Ber., ix, 810).

Green twigs of ligneous plants give off in the sunlight more gas than that corresponding with the volume of the twig; the portion evolved towards the end is almost pure oxygen.

C. S.

## Further Communications on the Diastatic and Peptone-forming Ferments in Plants.

By E. v. Gorup-Besanez (N. Repert. Pharm., xxv, 28—35).

After briefly referring to the work on flesh-eating plants done by Hooker and Darwin, the author considers it desirable that a more direct proof should be obtained of the solution and chemical metamorphosis of starch and albuminoïd bodies by the ferment-effecting materials of the germ in the endosperm.

This direct proof was originally confined to one plant, but the author is now able not only to maintain his original assertions after repeated tests of their accuracy, but also to show that the simultaneous occurrence of diastatic and peptone-forming ferments is by no means an isolated phenomenon in the vegetable kingdom.

The ferments in vetch, hemp, and linseed, in germinated barley, in kiln- and air-dried malt were examined. Ungerminated barley gave a negative result, which was to be expected, as diatase is formed only during germination; the interest lies in the fact that in the absence of diatase no peptone was formed.

To isolate the ferment, Hüfner's method was followed; after repeated precipitation, the vetch-ferment was obtained perfectly white and pulverulent. It remained active for weeks, and did not become coloured on exposure to light. It contained a large amount of ash (7·76 per cent.); a nitrogen determination made after deducting ash gave 4·3 per cent. N.

To prove if vetch ferment and coagulated albumin brought together in presence of very dilute hydrochloric acid would produce peptone, these materials were placed in a test-tube at the ordinary temperature of the room; after 24 hours, but still more distinctly after 48 hours, peptone could be clearly detected.

Peptone gives in a potash- or soda-ley containing a few drops of a very dilute solution of cupric sulphate, a pale rose colour; if the solution examined still contains unaltered albuminoïds, a violet-; and when it consists almost wholly of albuminoïds, a light-blue colour.

This reaction is very delicate; the chief precaution to be observed is the extreme dilution of the sulphate of copper solution.

Throughout the research verification experiments with fibrin and hydrochloric acid were made. Part of the fibrin went into solution; the filtrate was cautiously neutralised with ammonia, and on adding potassium ferrocyamide the so-called neutralisation precipitate (Meisner's syntonin and parapeptone) was obtained; no peptone was discovered. On adding the vetch ferment to the same filtrate from fibrin and hydrochloric acid, and treating it the same way, no unchanged albuminoïds could be found, but it gave the characteristic peptone reaction with great distinctness.

Quite recently a view has been put forward to the effect that pancreas peptone is only a combination of leucine, tyrosine and two other decomposition-products of albuminoïds. To test this, 300 grms. of fibrin, vetch-ferment and hydrochloric acid, as before, were taken; after several days the filtrate was treated with acetate of lead, and the lead precipitated with the filtrate evaporated on the water-bath to a syrupy consistence; after months' standing no deposition was observable; but when alcohol was added in large excess, a very finely divided precipitate fell, which eventually settled in an oily layer at the bottom; neither leucine, tyrosine, nor asparagine could be detected in it, but it gave a well marked peptone reaction.

With hemp and linseed similar results were obtained.

T. P. W.

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**Further Observations on Peptone-building Ferments in the Vegetable Kingdom.** By E. v. Gorup-Besanez and H. Will (Deut. Chem. Ges. Ber., ix, 673—678).

The authors confirm the statements of Hooker (*Nature*, x, ccclii, 366) on the digestive power of the secretion of *Nepenthes*. They found the liquid taken from unirritated glands to have a neutral, and that from the irritated glands an acid reaction. The latter acted upon fibrin, raw flesh, white of egg, legumin, and ossein, but not upon starch. The neutral liquid had no appreciable action on fibrin alone, but dissolved it at once on addition of a drop or two of formic acid. Acetic, propionic, malic and citric acids produce the same effect, but not to the same extent as formic acid. One of the authors had previously detected formic acid (and probably propionic or butyric acid) in the glands of *Drosera rotundifolia*. The conclusion is that the acid secretion in the cups of the different varieties of *Nepenthes* is a true vegetable pepsin.

G. T. A.

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**On the Development of Organisms in the Absence of Free Oxygen.** By Gustav Hüfner (J. pr. Chem. [2], ix, 475—479).

The author, in the course of experiments made with another object, has arrived incidentally at a result which, he thinks, definitely settles the vexed question as to the possible existence of living organisms in the absence of oxygen. He boiled water containing fibrin in flasks of

about 350 c.c. capacity, having long necks, of which the upper halves were bent at right angles to the lower. Near the mouths of the flasks the necks were contracted, so that they could be easily sealed. Into the neck of each flask, between the bend and the mouth, was fused a short capillary tube closed at the outer end, in which there was placed before boiling a small quantity of a putrefying liquid. The water in the flasks was boiled briskly for about three hours, and the flasks were sealed, the issuing steam having passed over the open ends of the capillary tubes and swept out air, without strongly heating the contents. After cooling, the flasks (which were quite free from air) were inverted so as to mix the putrefying liquid in the capillary tubes with the contents of the flasks. They were then kept at a nearly constant temperature of about 30° for a fortnight, at the end of which time they were found to contain gas, and the originally clear liquid had become turbid and coloured. The gases were extracted by means of a mercury pump. One flask contained 25 c.c. of gas consisting of 57·34 p.c. carbon dioxide and 42·66 p.c. hydrogen: another contained 22·7 c.c. of gas consisting of 77·72 p.c. carbon dioxide and 22·28 p.c. hydrogen. The liquid in the flasks abounded in bacteria, living and dead.

J. R.

**On the Nature of the Mineral Substances Assimilated by Mushrooms.** By L. CAILLETET (Compt. rend., lxxxii, 1205—1206).

THE ash of mushrooms differs considerably in composition from that of plants containing chlorophyll, probably owing to the method in which they are fed. A piece of wood on which a fungus had grown had lost almost all its mineral constituents, except an excess of lime and magnesia, and this disintegrates the wood completely. Analyses are given of some French mushrooms, and these show that mushrooms would make excellent manure owing to the amount of alkalis and phosphoric acid they contain. "Fairy-circles" are easily explained by the fact that a mushroom spore extends numerous rays, and forms a definite circle. In winter it dies, and the soil is manured at the place, and produces more healthy grass than the neighbouring earth. At the circumference of this circle, the germs revive in the subsequent spring, and extend still further into the adjacent earth. The mycelium draws almost all its alkalis and phosphoric acid from the soil. Silica is not found in mushrooms.

W. R.

**The Composition of Palm-nut Cakes.** By J. LEHMANN (Dingl. polyt. J., ccxix, 92).

THE author gives the following numbers showing the composition of these compressed residues of the palm-nut, the fruit of the oil-palm ("*Elais guineensis*") which grows on the African west coast, and in Central America. Palm-nut-cakes, of the following years, contained:—

| | 1872. | 1873. | | | 1874. |
|---|---|---|---|---|---|
| *Fat* | 15·14 | 14·47 | 14·34 | 14·23 | 8·45 |
| *Proteids* | 20·25 | 15·95 | 16·14 | 16·96 | 12·85 |
| *Extractive matters not containing nitrogen* | 22·51 | 29·20 | 32·99 | 34·72 | 50·58 |
| *Vegetable fibre* | 25·55 | 25·16 | 22·53 | 20·36 | 12·86 |
| *Ash* | 4·20 | 3·46 | 2·79 | 4·08 | 4·11 |
| *Water* | 12·35 | 11·76 | 11·21 | 9·65 | 11·15 |
| | 1875. | | | | |
| *Fat* | 9·98 | 9·82 | 7·19 | 10·55 | 8·50 |
| *Proteids* | 17·62 | 16·75 | 15·43 | 15·50 | 17·00 |
| *Extractive matters not containing nitrogen* | 39·30 | 42·73 | 49·58 | 40·27 | 31·19 |
| *Vegetable fibre* | 18·58 | 16·79 | 13·39 | 18·40 | 28·50 |
| *Ash* | 4·28 | 4·30 | 3·91 | 4·01 | 4·41 |
| *Water* | 10·24 | 9·61 | 10·50 | 11·27 | 10·40 |

The diminution of the fatty matter in later years is owing to recent improvements in the mode of extraction, viz., the application of greater heat and pressure. The author believes that this diminution has reached its extreme limits, and proposes that the farmer should ask a guarantee, in purchasing palm-nut cakes, of 15 per cent. proteids and 8·5 per cent. of fat. Cocoa-cake, the compressed residue of the nut of the cocoa-palm ("*Cocos nucifera*"), contains on the average even more proteids. Thus:—

| | Lehmann. | Kuhn. | Henneberg. |
|---|---|---|---|
| Fat | 22·6 | 18·5 | 16·6 |
| Proteids | 20·4 | 17·2 | 19·3 |
| Nitrogen-free extractive matter. | 28·9 | 32·2 | 30·2 |
| Vegetable fibre | 11·5 | 17·8 | 17·2 |
| Ash | 5·4 | 3·7 | 4·9 |
| Sand | 1·3 | — | — |
| Water | 9·9 | 10·6 | 11·8 |

W. S.

## Analytical Chemistry.

### Detection of the Mineral Acids by means of Colchicine.

By F. A. Flückiger (N. Repert. Pharm., xxv, 18—23).

Mohr has observed that under certain conditions the behaviour of inorganic acids differs totally from that of the organic; this difference may be utilised for their discovery in presence of organic acids, for example, in vinegar or lemon-juice.

Potassium sulphocyanate in a dilute solution of ferric acetate causes no change, but if there be the smallest trace of hydrochloric, nitric, or sulphuric acid present, the blood-red colour of ferric sulphocyanate is at once apparent: this, however, quickly vanishes on the addition of an acetate or oxalate; but in this case phosphoric acid acts like the organic acids in preventing the formation of ferric sulphocyanate. Another of Mohr's methods depends on the fact that iodine is precipitated from a solution of potassium iodide if a ferric salt with an inorganic acid radicle be added. Ferric acetate causes no precipitation in a solution of potassium iodide, but if the smallest trace of an inorganic acid be present the iodine is immediately precipitated.

But there is a case the reverse of this, in which the inorganic retards and the organic acid hastens the reaction. A solution of pure ferrous sulphate mixed with a saturated solution of gallic acid produces no change if the air be excluded, but acetates immediately produce in it a violet colour.

Still more remarkable effects are produced by colchicine. Some colchicine was extracted from a few grams of the seeds by means of alcohol and water, the yellowish solution was diluted till the colour was scarcely perceptible.

With concentrated sulphuric or nitric acid it gave a very distinct yellow, and on adding a drop of hydrochloric acid to this solution a bluish-violet was produced.

If some colchicine solution with a drop of nitric acid is strongly concentrated and then a fragment of sodium acetate added, an orange colour is formed.

If to a portion acidulated with sulphuric acid, a mixture of iodide of potassium and iodide of mercury in the proportion of 50 to 13·5 is added, a precipitate is formed; by means of this solution it was easy to detect ½ a per cent. of sulphuric acid in vinegar.

T. P. W.

**On some Reactions of Iodine and Palladium Chloride with Potassium Ferrocyanide.** By SERGIUS KERN (Chem. News, xxxiii, 184).

IODINE dissolved in alcohol when mixed with aqueous solutions of potassic ferro- or ferricyanide could neither be detected therein by starch nor precipitated by palladious chloride. The separation or estimation of iodine cannot therefore be made by palladium salts in presence either of potassic ferro- or ferricyanide. Bromine also is soluble in solution of potassic ferrocyanide. Palladious chloride gave a green coloration with potassic ferrocyanide similar to that produced by auric chloride.

F. J. L.

**A simple Method of Nesslerising.** By OTTO HEHNER (Chem. News, xxxiii, 185).

THE nesslerising is conducted in graduated cylinders, having glass taps fused into their sides so that the solution may be run out of either standard or distillate until the two colours correspond.

F. J. L.

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**An Estimation of the Free and Albuminoïd Ammonia yielded by the Stagnant Waters of the Dublin Streets, as compared with the Quantities of those Substances obtained from the Liffey Water after receiving the Sewage.** By L. STUDDERT (Chem. News, xxxiii, 185).

THIS comparison shows that the street waters contain in some instances several hundred times the quantity of free ammonia found in the river water. The author points to its sanitary influence.

F. J. L.

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**Determination of Glauber's Salt in a Bitter Salt (Magnesium Sulphate) Adulterated therewith.** By F. ANTHON (Dingl. polyt. J., ccxx, 467—468).

BITTER salt has the property of giving to water a spec. grav. which is considerably higher than that obtained with Glauber's salt. This property is noticed even when both salts are in the anhydrous state. A solution of bitter salt which, *e.g.*, contains 10 p. c. of anhydrous salt has a density of 1·1053, whereas a 10 p. c. solution of anhydrous Glauber's salt possesses a gravity of 1·0917. This difference in behaviour of the two salts is sufficiently marked to be employed for investigating an adulteration of bitter salt with Glauber's salt. About 20 grms. of the salt under examination are heated in a dish to 200° —250° until the whole of the water has been driven off; 10 grms. of the residue are now dissolved in 90 grms. of water, the temperature is brought to 15°, and the spec. grav. tried with the bottle. If the density is 1·1053 the salt under examination is pure bitter salt; if, however, the gravity is found to be 1·0917 the salt is nothing but Glauber's salt.

Between these two limits the various possible adulterations take place, so that, *e.g.*—

| A specific gravity of | Corresponds | | With the following percentage contents of Bitter salt. |
|---|---|---|---|
| 1·09170..... | ,, | ..... | 0 |
| 1·09306..... | ,, | ..... | 10 |
| 1·09442..... | ,, | ..... | 20 |
| 1·09578..... | ,, | ..... | 30 |
| 1·09714..... | ,, | ..... | 40 |
| 1·09850..... | ,, | ..... | 50 |
| 1·09986..... | ,, | ..... | 60 |
| 1·10122..... | ,, | ..... | 70 |
| 1·10258..... | ,, | ..... | 80 |
| 1·10394..... | ,, | ..... | 90 |
| 1·10530..... | ,, | ..... | 100 |

D. B.

**Volumetric Method of Estimating Aluminium Sulphate and Alum.** (Dingl. polyt. J., ccxx, 229—232).

THE principle of this process is as follows:—To the boiling solution of the aluminium sulphate so much titrated soda solution is added, that a very faint alkaline reaction remains permanent, which point is ascertained by using a solution of corallin (aurin) as indicator. Thus, $\frac{23}{24}$ths of the acid in the aluminium sulphate are abstracted, so that the precipitate which arises contains 8 atoms of alumina for each atom of sulphuric acid. Should the aluminium salt contain free sulphuric acid the quantity of the latter must be determined and be checked by the alumina determination. This estimation was made by using a $\frac{1}{10}$th soda solution with logwood solution as indicator. The delicacy of the hematoxylin reaction with free acids contained in aluminium sulphate is already known. If ferric oxide be present in the aluminium salt it is prejudicial to the accuracy of the estimation, and must be eliminated by precipitation with potassium ferrocyanide.

W. S.

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**Detection of Ethyl Alcohol in Mixtures, especially in presence of Wood Spirit.** By A. RICHE and CH. BARDY (Compt. rend., lxxxii, 768—770).

SOME aldehydes, together with such substances as methylal, acetal, &c., change the colour of solutions of rosaniline salts to a violet, which is not destroyed by the subsequent addition of sulphurous acid. Since methyl aldehyde is capable of being formed only under special conditions, it was thought probable that ethyl alcohol might be detected after oxidation, even in presence of methyl alcohol, by utilising the above reaction to show the formation of ethyl aldehyde.

It was proved that when methyl alcohol was distilled with potassium permanganate and sulphuric acid, the distillate did not affect the colour of a rosaniline salt.

About 4 c.c. of the liquid to be examined are placed in a flask with 6 c.c. of ordinary sulphuric acid and 10 c.c. of water; 7 or 8 c.c. are then distilled over into 10 c.c. of water; and to this liquid 5 c.c. of sulphuric acid, together with 10 c.c. of solution of permanganate of 4° B. are subsequently added. After five minutes have elapsed, 4 c.c. of solution of sodium thiosulphate of 33° B. and 4 c.c. of solution of magenta (·02 grm. per litre) are added. Under these conditions wood-spirit unmixed with ethyl-alcohol gives a yellowish-white liquid, but if ethyl-alcohol is present the solution assumes a violet colour, the intensity of which necessarily varies with the quantity of aldehyde formed.

Acetone, formic acid, and isopropyl alcohol give no coloration; moreover, while normal propyl-, isobutyl-, and isoamyl-alcohols are not found in commercial wood spirit, their aldehydes under similar circumstances affect rosaniline in a manner totally different from that of ethyl aldehyde, and do not produce a violet coloration.

The presence of alcohol may also be detected in water by means of this reaction; according to the authors the sensibility of the test is sufficient to detect one part of alcohol in 1,000 parts of water.

J. W.

## A Reaction for Distinguishing Alizarin from Extract-red.

By T. WAGNER (Dingl. polyt. J., ccxx, 444—445).

ON treating a real steam-red on cotton with a thickened solution of potassium ferricyanide (100—200 grms. per litre), and passing the cotton through dilute soda-lye, sp. gr. 1·027, then through boiling water and finally through soap-solution, the red undergoes no change of colour, but if the same red was prepared with madder-extract, it will alter its colour very much if exposed to these reagents. Wagner assumes that this distinction is due to the purpurin contained in madder-extract, an assumption which has been proved by direct experiments undertaken by Brandt and Dupúy. A red or violet dye, *e.g.*, with alizarin No. I of Meister, Lucius, and Co., remained perfectly intact when exposed to the above reagents.

D. B.

## The Detection of Eosin on Dyed Fabrics.

By R. WAGNER (Dingl. polyt. J., ccxx, 182).

BAEYER has shown that eosin can be detected by its ready conversion into fluorescin when it is treated with sodium amalgam. The bromine of the eosin is thus abstracted and fluorescin formed, giving in a very dilute solution its characteristic uranium-green fluorescence.

For the examination of red fabrics, Reimann's *Färberzeitung* recommends a concentrated aqueous solution of one part of aluminium sulphate in four of water, in which the coloured pattern must be warmed. Whilst such red colouring matters as the cochineal and logwood lakes and the tar colours, "fuchsine," "coralline," and "safranine" are extracted by this solution from the material, the eosin-red remains almost completely untouched. In order to test eosin for the presence of the above-named three coal-tar colours, as adulterations, it is best to use sulphuric acid diluted with four times its volume of water. In this, eosin is precipitated as an orange-red powder, whilst fuchsine and coralline with a yellow, safranine with a blue solution, remain dissolved.

R. Wagner has lately recommended a new and easy method of testing eosin. A solution of eosin and methyl-eosin treated with collodion is at once decolorised, whilst all aniline colours, Magdala-red and alizarin, are intensely coloured by collodion. The material is therefore dotted over with collodion by means of a glass rod, when a white spot is left at each point of contact if the colouring matter be ordinary or methyl-eosin. Wagner also points out that pyroxylin (gun-cotton), which readily takes up the aniline colours, is scarcely coloured by eosin.

W. S.

## On a New Apparatus for the Estimation of Fat in Milk, and Contributions to the Chemistry of Milk.

By N. GERBER (Deut. Chem. Ges. Ber., ix, 656—659).

DILUTE acetic acid is added drop by drop to 10 or 20 c.c. or grams of milk diluted with 20 to 30 times its volume of distilled water. The

beaker containing the liquid is placed in water at 75°, and left till the casein separates from the serum in large flocks; the liquid is then passed through a filter and dried at 110°. The serum is next evaporated down to one-quarter of its volume, and the albuminates obtained are added to the casein, and the mass is washed with cold distilled water till it loses its acid reaction. The liquid obtained is used for the estimation of the sugar. The albuminates are brought into a funnel-shaped vessel which fits on to a flask, and washed with alcohol. The liquid obtained is mixed with ether in the flask, and the funnel-shaped vessel is connected with an upright tube provided with a Liebig's condenser. When the apparatus is placed on a water-bath, the ether is distilled and passes up through the albuminates, and being condensed falls back and passes through the mass back into the flask, bringing the fat with it. Figures of the apparatus accompany the paper.

To estimate the quantity of water in condensed milk, a certain quantity should first be dissolved in a little water and mixed with a sufficient quantity of dried and weighed sand, evaporated on the water-bath, and then at 110° on the air-bath. The casein and albumin are found by dissolving the milk in tepid, not hot water, diluting with cold water, and proceeding as above. Addition of a trace of ammonium nitrate is found useful on incinerating for the estimation of salt.

G. T. A.

**Tests for the Adulteration of Food and Drink.** By A. Hilger (N. Rep. Pharm., xxv, 216—218).

*a. Commercial Vinegar.*—A large number of samples were found to contain only between 1 and 3 per cent. of pure acetic acid, whereas vinegar should contain at least 3 per cent. of pure acid. Sulphuric acid was mostly found, some qualities of vinegar containing as much as 1 per cent. of it. The free acid was detected as follows:—10—20 c.c. of the vinegar were concentrated to a syrup in a dish on a water-bath, and a small piece of sugar added, when the blackening of the latter showed the presence of free acid. Quantitatively the acid was determined as $BaSO_4$. For determining the free acetic acid in presence of free sulphuric acid, the author carefully neutralises 20 c.c. of the vinegar with standard potash (1 c.c. = 0·060 acetic acid). The number of potash c.c. used is at present only noticed, as a direct calculation of free acetic acid cannot possibly be made. The sulphuric acid is next determined as $BaSO_4$, and the acid found, calculated on the potash. The quantity of potash belonging to sulphuric acid is now deducted from the original quantity used for neutralisation, and the remainder calculated as belonging to free acetic acid.

*b. Milk.*—About 300 samples of milk were examined, all of which showed as adulteration nothing but water, often 20—30 per cent., and even as much as 40 per cent. The author recommends Quévenne's lactodensimeter and Chevallier's cremometer as being very useful instruments for the detection of additions of water to milk, and for ascertaining whether milk is skimmed or not skimmed.

*c. Adulteration of Spices.*—Samples of pepper showed additions of roasted powdered acorns, meal of leguminosæ, starch, various inorganic substances in powder, &c.

D. B.

## The Fraudulent Coloration of Wines. By A. GAUTIER (Bull. Soc. Chim. [2] xxv, 435—445).

*The Colouring Matters employed in the Adulteration of Wines.*—The substances mostly used at the present time to freshen or increase the natural colour of red wines, or sometimes to colour white wines, are—

1. Petals of the hollyhock (*Altha rosea*), variety *nigra*, which afford an extract of a fine deep wine-violet colour.
2. *Elder berries* (*Sambucus nigra*) and *S. Ebulus*. The tone of the extract is heightened with tartaric acid or with alum. The juices of both varieties are purgative in moderate doses.
3. *Privet berries* (*Ligustrum vulgare*).
4. *Portugal berries* (*Phytolacca decandra*). The juice of these berries yields a drastic purgative, on which account their use is now almost abandoned.
5. *Whortleberries*. Used almost exclusively to colour white wines, in Paris, but chiefly in Switzerland.
6. *Decoction of red beetroot*. Seldom employed alone, its chief use being to mask the tints of cochineal and of fuchsine.
7. *Logwood*. Chiefly used in Paris for common wines. One variety closely resembles the reactions for Brazil wood.
8. *Brazil wood* (alcoholic extract of).
9. *Cochineal* (carmine, carmine lake, ammoniacal carmine). Very largely employed, chiefly in Central France, to raise the tint of wines, themselves used frequently to adulterate the wines of Bergundy and Bordeaux. It is generally sold in thick solution in ammonia, or in cakes made by wetting the cochineal with ammonia, and then pressing it.
10. *Fuchsine, aniline reds*, and *violets* (not unfrequently contaminated with arsenic) are used in large quantities, either alone or with yellow or red substances, to diminish the brilliancy of their tints.
11. *Grenat*. A bye-product in the manufacture of fuchsine, consisting of a mixture of mauvaniline, chrysotoluidine, fuchsine, and an undetermined matter called brown grenat. Considerably employed.
12. *Indigo-carmine*, or *Ceruleine*, in paste. Somewhat largely used in Central France, chiefly for common wines.
13. A few substances sold under fantastic names, such as "colourine," "caramel," "colouring fluid," which generally consist of residues of fuchsine mixed with beetroot extract, carmine, &c., &c.

The greater part of the artificial colouring matters communicate a rose-red, or rich violet tint to the wines, which is mostly fugitive; moreover the majority of them soon separate and carry with them a portion of the natural colouring matter: this is particularly noticeable when cochineal, indigo, or fuchsine are the adulterants.

REACTIONS CHARACTERISTIC OF THE NATURAL COLOURS OF WINES.—The reactions vary somewhat with the products of various vines and with the age of the wines.

The following apply more especially to the wines of Central France, of Burgundy, and the Gironde, examined as usually sold, about five to eighteen months after the vintage.

*Carbonate of Soda.**—5 c.c. of a 1-200th solution of disodium carbonate added to 1 c.c. of natural wine afford a greenish-grey, green, or bluish-green colour. In certain sorts a winey or lilac tint remains, even with an excess of the reagent; another, *teinturier*, gives a deep bluish-green tint, which becomes chestnut-brown on heating.

The following reactions were performed on wine clarified (by a process to be explained subsequently) or else diluted with five or ten times its volume of water, so that it had only a rosy tint. The changes of colour should be observed about two minutes after the addition of the reagent.

*Bicarbonate of Soda charged with Carbonic Acid.*—8 per cent. by weight solution. Equal volumes of wine and of this reagent afford a slightly cloudy iron-grey liquid, with tint of bottle-green. *Teinturier* becomes deep green; *aramon* rose winey-brown; *aramon* with *petit Bouschet*, lilac, changing at 100° to the colour of extract of tea.

*Borax.*—Saturated solution at 15° B. 1 vol. of wine with 2 vols. of the reagent becomes bluish-grey or blue-grey, slightly greenish (*pinot*, 16 months old, *carignane*, 5 months old), or greyish-blue with trace of violet (*carignane*, 18 months), or entirely wine-lilac (*aramon* alone, or mixed with *petit Bouschet*). The colours should be viewed by transmitted light reflected from a white surface. They last several hours unchanged.

*Ammonia.*—10 parts of ordinary ammonia with 90 of water. The deeply coloured wines of Central France mixed with an equal volume of this dilute ammonia change to greenish-grey, bottle-green, greenish-yellow, or greenish-grey-blue. With *aramon* (of which the colouring matter differs most from that of the generality of wines) or a mixture containing it, the change is to buff, with trace of lilac. With new wine the change is more decidedly green, but alters subsequently to brown. If the wine is very dark coloured, one drop of a stronger ammonia causes a blue coloration or precipitate, which then changes to greenish or brown.

*Sulphide of Ammonium.*—10 c.c. of ammonia, with 8 c.c. of ordinary sulphide of ammonium made up to 1 litre with water. Equal volumes of wine and reagent are mixed and filtered. The filtrate is greenish with pure wines, but bluish or violet-lilac with those adulterated. The reaction is not satisfactory.

*Baryta-water.*—Saturated solution. Equal volumes of clarified or diluted wine and of this reagent afford on filtration an olive-green filtrate; sherry coloured with *teinturier* or *aramon*. This filtrate becomes rose on acidification with acetic acid, except with *teinturier*, which remains buff, and *aramon*, which becomes clear yellowish-green. It becomes red-brown or yellow-brown with logwood or Brazil wood.

* In the preparation of the reagents the instructions given must be strictly followed, in order to avoid errors otherwise certain.

*Subacetate of Lead.*—2 c.c. of wines with 1 c.c. of solution of subacetate of lead at 15° B. give variously coloured precipitates, which, however, afford no indication of the nature of the colouring matters. The filtrates from the precipitates are colourless with wines and most vegetable colouring matters, but rose or lilac with Brazil wood, and pale rose with fuchsine.

*Sulphurous Acid.*—Bleaches most vegetable colouring substances, but does not affect the colour of wines.

*Nascent Hydrogen.*—By the action of zinc and hydrochloric acid; affords no satisfactory reaction.

*Barium Peroxide.*—3 c.c. of clarified or diluted wine acidified with 5 drops of a 5 per cent. solution of tartaric acid, and treated with 0·1 grm. of barium peroxide is nearly decolorised in 24 hours. With elder (both varieties), fuchsine, Brazil wood, logwood, beetroot, cochineal, the colour remains for a much longer time.

REACTIONS FOR DISTINGUISHING MIXTURES OF WINE AND OF OTHER COLOURING MATTERS.—The first portion of this section is devoted to a review of the various methods suggested for detecting the foreign colouring matters, but none were found to be of any value practically.

A tolerably successful process is to steep in the suspected wine skeins of wool or silk variously mordanted, with such mordants as oxychloride of tin, alum with cream of tartar, and acetate of alumina. Certain differentiating reactions are thus obtained, but the process cannot be generalised. By mordanting scoured silk with tartaric acid, fixing the colour, and drying at 100°, after having acted upon it with various reagents, such as ammonia, lime-water, chlorides of zinc, iron, calcium, salts of copper, mercury, tin, some new reactions were observed which are characteristic of certain colouring matters.

C. H. P.

(*To be continued.*)

## Technical Chemistry.

### The Manufacture of Nitric Acid. By HUGO GÖBEL (Dingl. polyt. J., ccxx, 238—245).

PROPOSALS have been made, and methods devised for the decomposition of the sodium nitrate (Chili saltpetre), so that instead of sulphuric acid some other decomposing substance should be used, such as besides leaving behind a valuable residue, shall afford a good yield of acid. The best of these are the following:—

*R. Wagner.* Heating a mixture of alumina hydrate with sodium nitrate.

*J. Walz.* Heating sodium nitrate with calcium carbonate and steam in retorts.

*Kühlmann.* Heating sodium nitrate with manganese chloride, &c.

All these proposed methods have simply remained proposals, none

being found of sufficient merit as yet to replace the method by which nitre is decomposed with sulphuric acid.

However, the plant and apparatus used in the above universal method, have undergone from time to time considerable improvements. Thus the old, deep elliptical pans, with stone ware lids, &c., have been replaced by cast-iron cylinders, which are set up on their sides. These have been found to possess many advantages, as they require comparatively little fuel, are easily managed, and do not permit loss of gas at the joints, these being reduced to a minimum.*

Another improvement, now an old one, is the fractional distillation of the acid, by which means the production of a colourless concentrated acid was made possible. Then the old-fashioned earthenware head-piece and pipes were replaced by glass tubes, so that the reaction, and procedure of the distillation could be observed, and the danger of boiling or frothing over reduced or removed.

In earlier times, the receivers, consisting of earthenware or stoneware vessels, were frequently cracked and broken, with loss of vapours, or acid, or both. It was necessary to moderate the action very considerably, to prevent overheating of these condensers, and this meant loss of time, labour, and a reduced yield. To avoid these evils, R. Wagner proposed the employment of a series of funnel-shaped earthenware bottles, through which system the acid vapours circulate, accompanied by a stream of water. The author considers it questionable if the cooling of the distillate was sufficiently attained by these means. Another plan, to avoid the overheating of the receivers, was to allow the heated gases from the firing-up apparatus attached to the decomposing vessel, to pass under the condensers and so to warm them, before escaping to the chimney.

In England a still greater improvement was made, viz., the addition of a stoneware worm and condenser, through which the gases passed from the decomposer before entering the receivers. This precaution prevented the breaking of the receivers, or at least greatly reduced it. The apparatus used by the author with great success for cooling the gases, consists simply of a straight glass tube, bent at both ends, which lies in constantly renewed water. One end of the tube is connected with the tube of the decomposition apparatus, the other with the first receiver. This simple arrangement has enabled the author to decompose (with fractional distillation) 250 kilos. of saltpetre in 36 hours, and with no fractional distillation 300 kilos. in 36 hours.

Besides this, the receivers could be diminished in number from 9 to 3, most of the acid collecting in the first receiver. Also it is thus easy to obtain a very concentrated acid. Experiments showed that, in a cylinder apparatus, there were obtained in the first receiver 140 kilos. of acid of sp. gr. 1·53, temperature about 60°.

In the second, 55 kilos. of acid of sp. gr. 1·49.
In the last receiver the acid had a sp. gr. of 1·32.

In six months only one cooling-tube was broken. It is shown by numerical data given, that by this careful method of cooling, an

* *Note by Abstractor.*—These cast-iron cylinders are lined inside with fire-clay tiles, cemented with acid-proof cement.

increased production is obtained of 6·8 kilos. of acid of sp. gr. 1·33 per 100 kilos. of sodium nitrate.

At the end of the apparatus, *i.e.*, in connection with the last receiver, is placed a tower of earthenware tubes filled with coke soaked in concentrated sulphuric acid, by which means the nitrous gases, otherwise lost, are absorbed. In fact, the arrangement is simply a small Gay-Lussac's tower.

A useful table is given showing the increase of density of nitric acid on cooling from any likely temperature to 15·5° C.

| I. Temperature. | II. Increase on cooling to 15° in ° Baumé. | I. Temperature. | II. Increase on cooling to 15° in ° Baumé. | I. Temperature. | II. Increase on cooling to 15° in ° Baumé. |
|---|---|---|---|---|---|
| 45·0 | 3·65 | 35·0 | 2·10 | 25·0 | 0·90 |
| 44·5 | 3·56 | 34·5 | 1·98 | 24·5 | 0·80 |
| 44·0 | 3·48 | 34·0 | 1·92 | 24·0 | 0·76 |
| 43·5 | 3·40 | 33·5 | 1·85 | 23·5 | 0·72 |
| 43·0 | 3·32 | 33·0 | 1·79 | 23·0 | 0·67 |
| 42·5 | 3·23 | 32·5 | 1·73 | 22·5 | 0·63 |
| 42·0 | 3·15 | 32·0 | 1·67 | 22·0 | 0·59 |
| 41·5 | 3·08 | 31·5 | 1·62 | 21·5 | 0·55 |
| 41·0 | 3·00 | 31·0 | 1·56 | 21·0 | 0·52 |
| 40·5 | 2·92 | 30·5 | 1·50 | 20·5 | 0·48 |
| 40·0 | 2·85 | 30·0 | 1·45 | 20·0 | 0·45 |
| 39·5 | 2·73 | 29·5 | 1·34 | 19·5 | 0·36 |
| 39·0 | 2·65 | 29·0 | 1·29 | 19·0 | 0·33 |
| 38·5 | 2·58 | 28·5 | 1·23 | 18·5 | 0·29 |
| 38·0 | 2·50 | 28·0 | 1·18 | 18·0 | 0·25 |
| 37·5 | 2·43 | 27·5 | 1·13 | 17·5 | 0·20 |
| 37·0 | 2·36 | 27·0 | 1·08 | 17·0 | 0·13 |
| 36·5 | 2·29 | 26·5 | 1·03 | 16·5 | 0·07 |
| 36·0 | 2·23 | 26·0 | 0·99 | 16·0 | 0·05 |
| 35·5 | 2·16 | 25·5 | 0·94 | 15·5 | 0·02 |

Suppose for example an acid is examined and found to be of a specific gravity of 36° Baumé, and its temperature is 40°. If this be cooled to 15°, it will naturally become denser, and to the extent of 2·85° B., its density at 15° being 36 + 2·85 = 38·85° Baumé.

W. S.

## On Boiler Incrustations and their Prevention.

By F. Fischer (Dingl. polyt. J., ccxx, 172—181).

The following means have been recommended for avoiding or preventing the formation of boiler incrustations :—

1. By apparatus, contrivances and additions, which are introduced into the boiler itself, in order to protect its interior from the formation thereon of a solid incrustation.

By electricity.

Boiler deposit collectors, and contrivances which effect a rapid motion of the boiler water.

Iron turnings, sand and clay, &c.
Greasing and tarring the boiler sides.
Substances containing tannin, catechu.
Starchy matters, sugar, glycerin.

All the above means are condemned as at least useless, in many cases as only aggravations of the evil, or as exerting independent prejudicial action on the metal itself, as in the case of greases and fats.

Precipitations in the boiler.
Frequent blowing out.

II. By converting the incrustation-forming constituents of the water used for feeding the boilers, into soluble compounds, or precipitating them, before pumping the water into the boilers. The substances and methods recommended are :—

Hydrochloric acid, acetic acid, sal-ammoniac.
Barium chloride.
Heating in separate pans or boilers, before pumping in.
Milk of lime, or caustic alkalis.
Sodium carbonate or similar precipitants.
Simultaneous employment of several methods for purifying the water.

With respect to precipitations in the boiler, the use of barium chloride is recommended by several authorities (Kuhlmann, Hasenclever, von Reiche) as a precipitant for calcium sulphate, calcium chloride remaining in solution, and barium sulphate falling as a non-caking powder to the bottom of the boiler.

Varrentrapp asserts that if the barium chloride be not used in excess, so as to convert all calcium sulphate into chloride, there is danger of incrustation, from calcium sulphate yet undecomposed and barium sulphate already formed, these readily baking together to a solid mass. Vogel has found that when barium chloride is used as above, with water containing magnesium sulphate, barium sulphate and magnesium chloride are formed, and the latter, at the heat of the boiler, is then decomposed into magnesium hydrate and hydrochloric acid, which Vogel detected in the steam passing off.

If milk of lime be used for purifying water containing calcium bicarbonate, it should by no means be placed in the boiler itself, but the purifying process should precede the pumping into the boiler. The use of caustic soda, or sodium carbonate, is recommended by some eminent authorities, condemned by others. Kuhlmann and Fresenius recommend that soda be introduced into the steam boiler. Others complain that the plates are very strongly acted upon by it.*

With respect to frequent blowing out, with special contrivances and arrangements, by which too great concentration of the boiler water is

* *Note by Abstractor.*—The writer was acquainted with a case in which weak sodium hydrate liquors were boiled down to a specific gravity of about 1 20 in a steam boiler, the steam being thus made available and fuel economised. Examinations of the interior of the boiler always showed it to be extremely clean, quite bright, in fact, and completely free from the slightest vestige of incrustation. However this brightness and extreme cleanness is doubtless a suspicious circumstance. Any droppings from the gauge-taps on the heated metal outside, quickly covered the latter with a mass of rust.

prevented, it has been observed that much heat is lost, and so fuel wasted. Besides, when the deposits of boiler-stone have taken place, blowing out cannot remove them.

W. S.

**A Cheap Method of Evaporation suitable for Works-laboratories.** By W. A. C. THAU (Dingl. polyt. J., ccxx, 461—463).

THIS method is recommended for use in laboratories having easy access to a steam boiler. The apparatus consists of a long glass tube 26 mm. in diameter, to which three T-pieces are fixed, each having a metal cock. To the top of the latter copper pans are attached by means of screws. By placing the liquid to be evaporated on the pans, and allowing steam to pass through the tube, the steam will play on the evaporating vessels in a continuous stream, without superheating the liquid. The water condensing at the sides of the vessels runs down the pans and along a tube into the worm of a condenser. The latter is also connected with the end of the glass tube, so that by passing steam through it distilled water could be obtained. Solutions can thus be evaporated over night, as the apparatus requires no attention.

D. B.

**On the Physical Properties of Ordinary Waters.** By A. GÉRARDIN (Compt. rend., lxxxii, 1185—1187).

ALL varieties of water may be supposed to belong to one of two classes; blue water and green water. The blue water contains in suspension particles which have the Brownian motion, and thus do not settle to the bottom. It is a good drinking water. The green water contains organic matter, which may be seen, after the water has been evaporated, to consist of small unicellular algæ. Blue water is easily converted into green, by introducing organic ferment, but the reverse transformation is not practicable.

W. R.

**Crystallisation of Metallic Oxides from Glass.** By P. EBELL (Dingl. polyt., J., ccxx, 64—70 and 155—161).

THIS paper gives further details upon researches into the nature of glass (this Journal, 1875, p. 485), which seemed to show that glass when in a fluid state dissolves metals, which on cooling separate again in various forms, some being very crystalline. The oxides of tin, chromium, iron, manganese, and aluminium possess, under certain conditions, the property of giving crystalline deposits after having been absorbed by the fused glass, which must be attributed principally to the fact that the glass has been somewhat saturated with the metallic oxide and cooled slowly. On account of the greater resistance which these crystalline bodies offer to reagents, it was possible to isolate them and to investigate them analytically. All fusions were made in Hessian crucibles kept white hot in the coke fire of a blast furnace.

1. *Glass fused with Stannic oxide.*—A composition of glass from Hautefeuille was used, containing :—

| | | |
|---|---|---|
| Sand..... | 150·0 | grms. |
| Chalk ..... | 35·5 | „ |
| Calcined soda ..... | 80·0 | „ |
| Potash ..... | 14·0 | „ |
| Nitre ..... | 20·0 | „ |
| | 299·5 | |

A portion of this was fused with 20 grms. of stannic oxide, and gave on cooling a clear and transparent glass; but by fusing the same quantity with 60 grms., and cooling slowly, a colourless glass with crystalline deposits was obtained. These crystals, like those of chrome-aventurine (described below), resist the action of hydrofluoric acid, the fusion, separation, and purification being the same as in the case of the chrome-aventurine. For analysis the separated crystals had to be fused for an hour and a half with potash, in a silver crucible. The mass was then dissolved and the oxide precipitated with sodium bisulphate; 0·2432 grm. crystals gave 0·2470 stannic oxide or 101·6 per cent.

2. *Glass fused with Chromic oxide.*—Chromic oxide dissolves readily in fluid glass; if added in not too large an excess, a clear, transparent, green glass is formed, but if the oxide is added in larger proportions, a crystalline formation is obtained known under the name of *chrome-aventurine.* Pelouze states that 2½ p.c. of potassium bichromate gives no deposits on the cooled glass; however, 5 p.c. forms spangles, and 10 p.c. a perfect chrome-aventurine. The crystals are very distinctly formed, and can easily be distinguished by the eye. Under the microscope they appear in the form of flat plates with sharp angles and edges. In the experiment a composition of soda-lime glass free from lead was chosen; it contained—

5 parts of sand,
2 „ sodium carbonate,
1 „ lime.

After fusing the mixture, samples quickly drawn from the same and cooled seemed to show that the oxide had been completely dissolved; the mass was therefore cooled slowly in the crucible and was thus converted into chrome-aventurine. This was broken into small pieces and treated with hydrofluoric acid in the usual manner. The fused mass was next boiled with sulphuric and hydrochloric acids until the whole of the glass had been removed. The author did not forget to observe the progressive isolation of the crystals with the microscope. He found that the crystals did not suffer in the least during the whole operation. To prove that these crystals were chromic oxide, the author proceeded as follows: (1.) Fusing the mass with five times its weight of a mixture of equal parts of sodium carbonate and nitre, after having dried and weighed it. (2.) Dissolving the fused mass in dilute hydrochloric acid, evaporating to dryness at 105°, shaking up with dilute hydrochloric acid. (3.) Treating the mass with sulphurous

acid to reduce it, then precipitating with ammonia and weighing as chromic oxide.

0·1237 grm. chrome-aventurine crystals gave 0·222 grm. chromic oxide, corresponding with:

| | |
|---|---|
| Chromic oxide ..... | 98·79 |
| Loss..... | 1·21 |
| | 100·00 |

3. *Glass Fused with Ferric Oxide*.—A mixture of 450 parts by weight of glass (Hautefeuille) and 120 parts of finely powdered bloodstone free from admixtures gave, when fused for several hours, no deposits, even when cooled slowly. The fused mass was opaque, and almost black. The fusion was repeated with more iron, and after two trials the fourth fusion showed signs of crystalline separation when cooled slowly. The product, however, with regard to its physical properties could scarcely be called glass, for it had assumed a black colour and had lost its vitreous lustre. After digesting the mass with hydrochloric acid, silica remained behind. A portion digested with hydrochloric acid until the residue became colourless gave, on analysis, the following numbers:

| | | |
|---|---|---|
| Insoluble residue ..... | 41·33 | per cent. |
| Lime ..... | 4·21 | ,, |
| Alumina..... | 4·12 | ,, |
| Ferric oxide ..... | 41·03* | ,, |
| Alkalis ..... | not determined. | |

While the whole body presented to the eye a regular mass with crystalline structure thin layers of it showed under the microscope distinct signs of a light brownish-green mass of glass in which long crystals were embedded. Hydrofluoric acid dissolves the mass very easily, leaving the crystals in the form of a dark powder, soluble in concentrated hydrochloric acid. The crystals were isolated in this manner. They are strongly attracted by the magnet, appear under the microscope, and are very similar to powdered magnetic iron ore, and gave by analysis 71·37 p.c. Fe and 28·17 O., agreeing nearly with the formula, $Fe_3O_4$, which requires 72·41 Fe and 27·58 O.

A portion of the ferric oxide added to the glass had therefore formed a combination of monoxide and sesquioxide—a compound very constant to heat—and another portion had remained in the glass. Permanganate of potash (1 c.c. = ·00487 grm. of iron) was used to determine the proportion of ferrous and ferric oxide in the iron oxide obtained, and also to determine the stage of oxidation of the iron remaining in the glass. A portion of the fused glass was powdered, digested for several hours with hydrochloric acid until the residue turned colourless, carbonic acid being passed into the mixture to prevent the oxidation of the ferrous oxide. The solution of 1·015 grm. of glass required 9 c.c. of potassium permanganate to convert the ferrous into ferric oxide. The solution now contained the iron only as

* Equal to 28·72 per cent. of metallic iron.

ferric oxide; it was reduced with zinc and hydrochloric acid, and required 49·5 c.c. of standard permanganate of potash to oxidise the iron completely.

| Total. | As ferrous oxide. | As ferric oxide. |
|---|---|---|
| 23·80 p. c. | 4·31 p. c. | 19·49 p. c. |

corresponding with 17·85 p. c. of ferrosoferric oxide, besides 15·53 p. c. of ferric oxide.

4. *Glass fused with Manganese Dioxide.*—This glass was prepared by the addition of pyrolusite to ordinary glass, 150 parts giving no deposits with 450 parts of glass. By using a larger proportion of manganese, and cooling the glass, crystals of a peculiar form were obtained, which differed from those obtained in the experiments with the other oxides. The mass when split in halves showed two heterogeneous substances, one forming the outside, the other the inside or kernel of the block. The outer portion was black, striated, crystalline, like pyrolusite, opaque, and without lustre; the inner portion was regularly surrounded by the outer, had a light yellowish-brown colour, and showed faint signs of a crystalline structure, and a large quantity of black crystals like the leaves of fir trees, while the whole mass appeared opaque and not unlike some crystalline rocks. These layers, however, could not be separated by blows with a hammer. Under the microscope such differences were not perceptible; the black layer was resolved into a light transparent ground-mass, intergrown with black crystals, and therefore was the same microscopically as the flesh-coloured layer macroscopically.

After fusion with alkalis the crystals can be dissolved in mineral acids. 0·6835 grm. fused glass gave 0·318 silica, 0·0086 alumina, 0·021 lime, and 0·3035 sulphide of manganese. 1·063 light layer gave 0·488 silica, 0·0335 lime, and 0·440 sulphide of manganese; another sample = 1·321, gave 0·370 alkaline subchlorides with 0·2012 chlorine. These numbers converted into per cents. give—

| | Black layer. | Light layer. I. | Light layer. II. |
|---|---|---|---|
| Silica | 46·53 | 45·91 | — |
| Lime | 3·07 | 3·15 | — |
| Alumina | 1·26 | 1·24 | — |
| Manganese (metallic) | 28·08 | 26·05 | — |
| Soda | — | — | 7·65 |
| Potash | — | — | 8·56 |

0·292 grm. of the coarse crystals left on fusing a portion of the light layer with sodium bicarbonate, repeatedly boiling with water, and treating with dilute sulphuric acid, gave 0·296 $Mn_3O_4$, corresponding with 101·3 p. c.

5. *Glass fused with Alumina.*—The alumina necessary for fusion was prepared from ammonia-alum, by fusing it, and then washing the fused residue well with water until free from acid. Although large quantities of alumina were used in the first trials, deposits of crystals could be obtained only when equal parts of glass and alumina were fused together. The fused mass was not transparent, but formed a

translucent wax-like substance, of faint greyish-green tinge. Thin splinters appeared under the microscope, perfectly transparent, and were intergrown with colourless transparent crystals. The crystals were of two kinds, one forming thin, imperfectly developed laminæ, the other consisting of round, perfect, but smaller individuals. After treatment with hydrofluoric acid, a residue was left which, when purified with dilute hydrochloric acid, gave both the crystal forms above described free from admixtures. 0·6074 grm. of crystals fused with sodium bisulphate gave 0·606 alumina, corresponding with 99·85 per cent.

From the above experiments it appears that the oxides of tin, iron, manganese, &c., are absorbed by glass exposed to a white heat, forming a clear liquid, which, when cooled slowly, deposits a part of these metallic oxides in a crystalline form, but at the same time retains a portion of them, so that the added metallic oxide in its liquid state is either totally combined, and the separation is due to some chemical decomposition; or the oxide is only partly in a state of chemical combination, the excess being merely dissolved by the fluid glass. This latter assumption seems to be the most probable. If glass serves as a solvent for metals, why should it not dissolve oxides of metals as soon as the quantity of the latter exceeds that with which silicic acid can enter into chemical combination? If the whole of the oxide were chemically combined with the fluid glass, the capacity of the silica would not have fixed limits, but would vary with the temperature. The proportion of the crystallised part to that left in the glass, the colour of the glass, and the fact that the separation of the crystals depends not only upon temperature, but also upon time, give further proof in favour of a solution of the oxide rather than of a chemical combination. With regard to the nature of slags, and the formation of mineral silicates, these appearances are well worthy of notice in metallurgy and mineralogy. The practical uses derived from these experiments must be left to the consideration of manufacturers.

D. B.

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**Presence of Lead in the Platinum Points of Lightning Conductors.** By S. DE LUCA (Compt. rend., lxxxii, 1187—1189).

THESE points belonged to the lightning conductors on the observatory at Vesuvius, and were both melted into small globules. Their specific gravities were respectively 19·82 and 19·09 They contained respectively 9·5 and 12 per cent. of lead.

W. R.

**Persian Red (Chrome Red).** By A. PRINVAULT (Dingl. polyt. J., ccxx, 259).

NEUTRAL lead carbonate is digested with a cold dilute solution of neutral potassium chromate (1 part to 50 of water), so that one equivalent of the latter acts upon two of the former compound. Thus after two days a crystalline precipitate of basic lead chromate is obtained—

$$2PbCO_3 + K_2CrO_4 + H_2O = \underset{\underset{PbO}{\|}}{PbCrO_4} + 2KHCO_3$$

The supernatant fluid, consisting of potassium hydrogen carbonate, gives up a portion of its carbonic acid on boiling, and is converted into potassium carbonate, which decomposes a portion of the red precipitate, so that the latter assumes a violet-red tint, the solution itself a yellow colour. The composition of the precipitate now varies between $PbCrO_4.2PbO$ and $PbCrO_4.H_2O.PbO$, according to the concentration of the liquid. This violet-red precipitate, after being sufficiently washed, is treated with 4 per cent. of its weight of dilute sulphuric acid (1 part of sp. gr. 1·8426 to 100 parts water). The acid is added slowly, with continual stirring, and afterwards the whole is cautiously neutralised with dilute soda-solution, whereby a mixture of sulphate and dibasic lead chromate is obtained. The colour is now a bright vermilion, and this is the so-called "Persian red."

Nitric and acetic acids may be used instead of sulphuric acid as above, but in no case hydrochloric acid. The proportions recommended are 25 grms. of lead carbonate, and 10 grms. of neutral chromate, to be dissolved in 0·5 litre of water. This to be allowed to digest for two days in the cold, then boiled for half an hour, filtered, the precipitate washed, and treated with 1 grm. of sulphuric acid diluted with 100 parts of water.

"Persian red" will be chiefly useful as an oil-colour.

W. S.

## Use of Phosphoric Acid in the Sugar Manufacture.

(Dingl. polyt. J., ccxx, 190.)

SCHEIBLER has shown that by removing lime from the sugar-juice by means of phosphoric acid, many organic foreign bodies are also precipitated. Vibrans points out also, as other advantages of this process, proceeding from the removal of large quantities of organic matters, the easier working of the juice, its rapid evaporation, and its purer and larger yield of pure juice. The animal charcoal is also economised, whilst the phosphoric acid is easily recovered in the shape of a manure. According to Vibrans, beetroot sugar-juice was heated in the separating pan to 80°, and then 5 litres of phosphoric acid of 20° Baumé were added per 1,500 litres of juice; the temperature rose to 88°. Finally the solution was treated with lime and carbonic acid in the usual way.

The mud separating in the pan and settling down contained—

| | Without phosphoric acid. | | With phosphoric acid. | |
|---|---|---|---|---|
| Moisture | 50·85 | | 47·12 | |
| Carbonic acid | 10·22 | | 11·85 | |
| Sulphuric acid | 0·31 | | 0·22 | |
| Phosphoric acid | 0·27 | | 0·86 | |
| Ferric and aluminic oxides | 1·06 | | 0·33 | |
| Lime | 24·75 | | 16·13 | |
| Magnesia | 0·33 | | 0·47 | |
| Insoluble residue | 0·38 | | 0·10 | |
| Organic matter | 10·25 | | 22·30 | |
| Nitrogen therein contained | | 0·33 | | 0·52 |
| Residue and alkalis | 1·58 | | 0·62 | |
| | 100·00 | | 100·00 | |

Whereas the purified juice without use of phosphoric acid contained 4·07 per cent. of organic non-saccharine matter, that purified by phosphoric acid contained only 1·93 per cent. Gruber and Hulva noticed the value of the above method in the case of abnormal juices and beets which have begun to rot. Hulva took per 500 kilos. of beet 1 litre of phosphoric acid of 30 per cent. strength; but the suitable amounts for each case cannot as yet be fixed with certainty. Certain works in Silesia were brought to a stand, because the juice would neither settle nor filter, but the judicious use of phosphoric acid soon brought them again into full activity. Hulva maintains especially that those organic matters which render boiling difficult, and cause the formation of much molasses, are removed by the use of the above-described method.

W. S.

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## The Formation of Cheese. By F. Cohn (Dingl. polyt. J., ccxx, 191).

Blondeau found that in the making of Roquefort cheese, the casein can be converted into a fatty substance by the common mildew fungus (*Penicillium glaucum*). Cohn has made a series of inquiries into the changes occurring in the making of Swiss cheese, of which the following are extracts:—

The milk is treated in large copper pans with rennet-solution, a stiff gelatinous mass being obtained. The whole is left to itself for a quarter of an hour, and is then stirred up till the mass is broken into pieces about the size of a pea, when the pan is heated over an open fire from 55° to 60°, with stirring, for about an hour. The cheese paste is now separated from the whey by gradually increased pressure. The mass so obtained is placed in a cellar, where it can remain at a temperature of from 10° to 12°. Here the outside, or rind, is daily rubbed with salt, till the cheese goes into the warehouse, where it very slowly ripens.

The coagulation of the milk is accomplished unquestionably by an unorganised ferment present in the rennet-solution, for an alcoholic extract of rennet coagulates the milk quite as well as an aqueous

extract, and by a certain amount of the same only a corresponding quantity of milk is coagulated, whereas organised ferments increase and multiply themselves, developing an unlimited living power. The separation of the coagulated casein from the whey appears to be a purely mechanical process.

The ripening of the cheese, by which the white sweetish mass gradually attains the desired pungent taste and odour, the translucent consistency, and yellow colour, Cohn takes to be a genuine fermentation, which takes place under the influence of fermentation organisms. The fermentation begins whilst the cheese is yet on the press, in about 24 hours, and accompanied with lively evolution of gas (carbonic acid and probably other gases). In consequence of this gaseous evolution, the cheese swells, and its surfaces, which are even at first, become arched; its interior is also more or less perforated with holes, just as in the case of bread. The chemical phenomena which occur during the fermentation of cheese are as yet but little known. The author believes that the retention of whey in the cheese is advantageous, its lactose being converted by zymophytic fermentation into butyric acid. The "rennet" contains very active thread-bacteria (*Bacilli*), which probably induce butyric fermentation, and bring about the slow ripening of the cheese; their spores are those which are able to withstand the temperature of boiling water for some time, and again introduced into their own solution will develop once more into Bacilli, whereas the putrefactive bacteria which may be present are killed by merely warming the milk.

W. S.

## Utilisation of Human Excrements. By H. Schwarz (Dingl. polyt. J., ccxx, 161—171).

The process proposed by the author is briefly as follows:—The crude materials are mixed with milk of lime and heated in a closed boiler till a kind of separation takes place and the ammonia is volatilised. This ammonia is dried as far as possible and condensed and the separated mud filtered and pressed, the clear aqueous fluid being run off.

The manurial value of the excrements are stated as follows:—

1. The ammonia, combined mostly as carbonate, and arising chiefly from the fermentation of the urea. This fermentation and decomposition take place very quickly in presence of much of the urea-ferment. In winter this change may occur in twenty-four hours under this condition.

2. Combined nitrogen occurs in small quantity; what is present as urea and albumin goes into and along with the lime precipitate.

3. Phosphoric acid, present partly as calcium phosphate, partly as alkaline phosphate, passes off with the lime precipitate as calcium phosphate.

4. The potash alone remains soluble, and is lost in the fluid finally run off.

The following experiment was tried on a practical scale:—4 cwts. excrements were treated in a closed steam-chest with 3 per cent. of lime and the ammonia driven off: after cooling to condense, the steam

from it was condensed in sulphuric acid. The acid liquid was then weighed and the ammonia determined in a portion; this represented 0·36 per cent. of nitrogen in the fæces. The lime precipitate dried and expressed gave 8·37 per cent. of lime-manure with 0·96 per cent. of nitrogen, or 0·08 per cent. on 100 parts of fæces. The filtrate furnished on evaporation on 100 parts of fæces 1·48 per cent. of residue, with 4·06 per cent. of nitrogen. Thus—

| | | | |
|---|---|---|---|
| In the distillate was ..... | 0·36 | per cent. | nitrogen. |
| „ precipitate was..... | 0·08 | „ | „ |
| „ liquid filtrate was .... | 0·06 | „ | „ |
| Total..... | 0·50 | „ | „ |

In other experiments the following results were obtained:—

| | Obtained. In the distillate. | Obtained. In the precipitate. | Lost. In waste liquor. |
|---|---|---|---|
| Nitrogen, N ..... | 1·16 | 0·16 | 0·034 |
| Phosphoric oxide, $P_2O_5$ | — | 0·11 | — |
| Potassium oxide, $K_2O$. | — | 0·02 | 0·052 |
| Totals ..... | 1·16 | 0·29 | 0·086 |

Of the total manurial value as regards nitrogen 85·6 per cent. are gained, 14·4 per cent. lost. As regards the mode of collection of the fæces, the point of greatest importance, the author proposes what he terms the barrel system, whereby the solid and liquid constituents are both preserved. As regards quantity of fuel required for evaporation, boiling, &c., by economical arrangement of the plant for reducing this as much as possible, it was found that not more than 4 kilos. of coal for 100 kilos. of fæces would be required. The amount of lime also it is possible to reduce to about 2 per cent. of the fæces. About 6 per cent. of chamber sulphuric acid of 58 per cent. $SO_4H_2$ would be required.

The plan of operating on the large scale is briefly as follows:—The barrels are emptied of their contents at the works into a closed basin or reservoir of cemented brickwork, in which the matter remains for one or two days in order that the urea-fermentation may be fully completed. The semi-fluid matter is now pumped or run off into two cylindrical boilers, connected with each other in such a way that either may be directly heated, and when one is thus heated the steam from its contents may be allowed to pass into the contents of the other, thus heating them up to the boiling point. The boiler with contents furthest exhausted of ammonia is directly heated, the steam with final traces of ammonia passing into the contents of the other boiler. This boiler is now heated, its ammonia as far as possible driven over and condensed in the sulphuric acid; the course of the steam is then changed, and the process is finished by further boiling and distillation into the contents of the first boiler, which has now been replenished with a fresh charge, and so on. Both boilers are furnished with agitators, with perforated arms, to secure by their continual motion a

uniform mixture, and thus preventing caking of the precipitate and burning of the boiler bottom. The milk of lime is supplied from a pan also furnished with agitator and situated above the boilers. Each boiler has at the bottom a wide tap to let off the spent contents with rapidity, also safety-valve and glass to indicate the level of the fluid contents. There is also to be a smaller tap, from which samples may be drawn, to ascertain the degree of exhaustion and the completion of the distillation. The ammonia, with steam, is passed upwards through a coil of piping or worm with the object of condensing as much of the steam as possible; and in order that ammonia shall not also be absorbed and carried away by the water, the worm is carried up through a vessel used thus as a condenser, but containing warm water or other liquid; the ammoniacal gas now descends through a Liebig's condenser, being absorbed either by sulphuric or by hydrochloric acid. For manurial purposes it should be absorbed by calcium superphosphate. If required for liquor ammoniæ or ammonia solution, the gas is passed first through a cylinder filled with wood charcoal, to deoderise it before condensation in pure water.* The precipitate left in the boilers is placed in a filter-press, and the press-cakes obtained are dried by steam. The manurial value of this precipitate or boiler-residue is not great. It is expressed as follows:—

| | | |
|---|---|---|
| 1·21 | per cent. | nitrogen. |
| 3·75 | ,, | $P_2O_5$. |
| 0·52 | ,, | $K_2O$. |

The author expresses his willingness to assist any who take an interest in his process with further communications on the subject.

W. S.

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**Division of the Nitrogen of Barley among the Products of Brewing.** By F. Zmerzlikar (Dingl. polyt. J., ccxx, 70—75).

To ascertain how the nitrogen in barley becomes divided among the various products obtained therefrom, the nitrogen of various materials, products, and residues used and obtained in the brewing process had to be determined. The following is a list of the materials taken from Schilcher's brewery in Graz:—(1) Raw, untrimmed barley. (2) Soaked barley. (3) Water after being used for soaking. (4) Malt. (5) Malt sprouts. (6) Dust from trimming sprouts. (7) Unhopped wort. (8) Malt dough. (9) Returns. (10) Hops. (11) Hopped wort. (12) Hop returns. (13) Cooled lees (14) Yeast. (15) Young beer. (16) Lagerbier. In all these substances the hygroscopic water was determined and the nitrogen estimated in the dry product. The drying was partly made with steam, but partly also in air-baths at 100°. Barley malt and yeast (soaked) were dried at 20°—30° in the air. The water and the beer were evaporated to dryness and the thick syrup dried in a vacuum over concentrated sulphuric acid at 120°. The nitrogen was determined as ammonia with soda-lime, using normal oxalic acid as the receiving liquid.

* *Note by Abstractor.*—It would also in this case be necessary to pass the gas through a dry lime purifier, to free it more completely from moisture.

(1.) Barley from the Oedenburg district, Hungary, contained 11·30 per cent. of moisture, 1·605 per cent. of nitrogen on the dry substance, and 1·423 per cent. on the substance dried in the air, the latter corresponding with 8·999 per cent. of albumin; it also contained starch corresponding with 78 per cent. of sugar and 2·64 per cent. of ash.

(2.) Barley soaked and taken from the steeping-cistern after having been spread on the couch and left for eight hours. The adhering water was removed with blotting-paper, but the product still contained 41·11 per cent. of moisture. The nitrogen amounted to 1·252 per cent. on the dry, and 0·737 per cent. on the wet barley, the latter being equal to 4·696 per cent. of albumin.

(3.) The water, after having been used for soaking, had a yellowish-brown colour, was opaque, and had a slight smell. It left a residue of 0·1183 per cent. of solid, containing 1·456 per cent. of nitrogen or 0·00172 per cent. on the water.

(4.) Malt, as green malt, contained 42·62 per cent. of moisture. Dried in the air at 20°—25° it still showed 10·2 per cent. and at 48° 6 per cent. of moisture. At 100° it contained 1·694 per cent. of nitrogen. Dried slowly to 75° it gave 30·1 per cent. of sugar.

(5.) Malt sprouts contained 14·48 per cent. of moisture and 3·579 per cent. of nitrogen in the dry state, and 3·061 per cent. when dried in the air.

(6.) Dust from the trimmings mixed with small sprouts contained 13·569 per cent. of moisture and when dry 2·974 per cent. of nitrogen, but when wet 2·570 per cent.

(7.) Unhopped wort, sp. gr. 1·0493, equal to 12·119 per cent. saccharometer. The evaporated extract amounted to 12·251 per cent., containing 0·993 per cent. of nitrogen, corresponding with 0·1216 per cent. of nitrogen in the wort.

(8.) Malt dough contained 82·95 per cent. of water and 5·806 per cent. of nitrogen on the dry and 0·989 per cent. on the damp substance.

(9.) Returns contained 75·33 per cent. of water, and when dry 3·091 per cent., wet 0·762 per cent. of nitrogen.

(10.) Hops. A mixture of three kinds was used, which gave 11·05 per cent. of water and 1·826 per cent. of nitrogen when dried in air, but 2·053 per cent. of nitrogen when dried at 100°.

(11.) Hopped wort taken as it filtered through bags from the cooler, sp. gr. 1·0511 = 12·547 per cent. saccharometer. On evaporating 12·622 per cent. of extract is obtained, which gave 0·921 per cent. of nitrogen, corresponding with 0·116 per cent. on the wort.

(12.) Hop-residues contained 77·18 per cent. of water and 0·639 per cent. of nitrogen; when dry they contained 2·799 per cent. of nitrogen.

(13.) Cooled lees contained 77·55 per cent. of water and 5·300 per cent. of nitrogen when dry, and 1·190 per cent. when wet.

(14.) Yeast, after being washed and dried with blotting-paper, contained 76·47 per cent. of water and 1·913 per cent. of nitrogen; dried at 100° it contained 8·130 per cent. of nitrogen.

(15.) Young beer taken when ready for putting into casks: sp. gr. 1·0173. The alcohol obtained by distilling the beer to one half gave 5·50 per cent. on the distillate, or 2·75 per cent. on the beer. The beer con-

tained 5·62 per cent. of extract, containing 1·485 per cent. of nitrogen, equal to 0·083 per cent. on the beer.

(16.) Lagerbier, sp. gr. 1·016, gave 5·427 per cent. of extract, with 1·217 per cent. of nitrogen, equal to 0·066 per cent. on the beer.

Percentage composition of the results obtained:—

| Substances. | Nitrogen. (Dry at 100°.) | Moisture. | The moist substances contain. | |
|---|---|---|---|---|
| | | | Nitrogen. | Albumin. |
| 1. Barley | 1·605 | 11·30 | 1·423 | 8·999 |
| 2. Soaked barley | 1·252 | 41·11 | 0·737 | 4·696 |
| 4. Malt | 1·694 | 6·00 | 1·592 | 10·139 |
| | | 10·20 | 0·521 | 9·687 |
| | | 42 60 | 3·972 | 6·191 |
| 5. Malt-sprouts | 3·579 | 14·48 | 2·061 | 19·497 |
| 6. Dust | 2·974 | 13·57 | 0·570 | 16·371 |
| 8. Malt-dough | 5·806 | 82·95 | 0·989 | 6·301 |
| 9. Returns | 3·091 | 75·33 | 1·762 | 4·853 |
| 10. Hops | 2·053 | 11·05 | 0·826 | 11·630 |
| 12. Hop-returns | 2·799 | 77·18 | 0·639 | 4·067 |
| 13. Cooled lees | 5·300 | 77·55 | 1·190 | 7·578 |
| 14. Yeast | 8·130 | 76·47 | 1 913 | 12·185 |

| Substances. | Residue or Extract. | Nitrogen in Extract. | Nitrogen in the Liquid. | Albumin in the Liquid. | Alcohol in the Liquid. |
|---|---|---|---|---|---|
| 3. Water, after soaking | 0·118 | 1·456 | 0·0017 | 0·0108 | — |
| 7. Unhopped wort | 12·251 | 0·993 | 0·122 | 0·774 | — |
| 11. Hopped „ | 12·622 | 0·921 | 0·116 | 0·741 | — |
| 15. Young beer | 5·620 | 1·485 | 0·083 | 0·531 | 2·75 |
| 16. Lagerbier | 5·427 | 1·217 | 0·066 | 0·420 | 3·23 |

36 cwts. of barley were soaked. The skimmed barley amounts to 54 lbs., *i.e.*, 1·5 per cent. on the raw barley. The water weighs 98 cwts. 72 cwts. of barley gave 53·3 cwts. of malt (dried at 37°—50°). Thus a loss of 25·5 per cent. takes place, 100 parts of barley giving 74·5 parts of malt. For 22 cwts. of this malt 63 pails (at 56·6 litres) of warm water are used and afterwards 27 pails of water added, thus 84 pails of wort of 12·2 per cent. saccharometer (1 pail equals 42·5 Vienna measures at 1·415 litres) are obtained, 1 pail of wort weighing 112 lbs. To this 24 lbs. of hops are added and 18 lbs. of pappy yeast used as settling-yeast. From this 85 pails of beer, at 102 lbs. per pail, are obtained.

The skimmed barley amounts to 1·5 per cent. on the raw barley, *i.e.*, 46 87 lbs. for one brewage. The malt-sprouts amount to 108 lbs., equal to 3 per cent. of the barley. The dust from trimming the

sprouts is estimated at 18 lbs., or 0·5 per cent. on the raw barley, the returns at 29·26 cwts. in their wet state, the dough at 5 cwts., the cooled lees at 150 lbs., the hop-residues at 120 lbs., the yeast at 162 lbs. 85 pails of beer at 102 lbs. weigh 86·70 cwts. The nitrogen of raw barley would therefore have to be divided as follows:—

| Total weight of substances. | Materials, Products, and Residues. | Nitrogen. | Weight of Nitrogen. | 100 parts of the Nitrogen in barley correspond with. |
|---|---|---|---|---|
| Pounds. | | Per cent. | Pounds. | Per cent. |
| 3125·00 | Raw barley ..... | 1·4230 | 44·468 | 100·00 |
| 46·87 | Skimmed ditto ..... | 1·4230 | 0·667 | 1·50 |
| 9800·00 | Water, used ..... | 0·0017 | 0·169 | 0·38 |
| 108·00 | Malt-sprouts ..... | 3·0610 | 3·306 | 7·43 |
| 18·00 | Dust ..... | 2·5700 | 0·463 | 1·04 |
| 2926·00 | Wet returns..... | 0·7620 | 22·313 | 50·18 |
| 500·00 | „ dough ..... | 0·9890 | 4·947 | 11·12 |
| 150·00 | „ cooled lees ..... | 1·1900 | 1·785 | 4·01 |
| 120·00 | „ hop-returns ..... | (0·639) | *0·219 | 0·49 |
| 162·00 | „ yeast..... | 1·9130 | 3·099 | 6·97 |
| 8670·00 | Lagerbier ..... | 0·0660 | 5·722 | 12·87 |
| ? | ? | ? | 1·778 | 4·01† |

D. B.

## Carbon Sulphide as a Disinfectant. By P. Zöller (Deut. Chem. Ges. Ber., ix, 707—710).

Carbon sulphide is a very powerful disinfectant and may be used with advantage for preserving articles of food and other organic substances. Thus, on hanging pieces of veal and beef weighing 250—1,000 grms. in bell-jars containing a basin with some carbon sulphide and standing on a plate containing water, the meat remained unchanged for 32 days at 15°—24°. Fowls and pigeons which were embowelled and partly plucked, partly not plucked, kept equally well, and freshly baked hot bread placed in moist air containing vapour of carbon sulphide did not become mouldy in 14 days. Over-ripe plums were kept without change for 192 days, while the same fruit when kept in air confined by an indigo-vat began to decompose in a few days. Sulphide of carbon vapour stops the fermentation of a sugar-solution and prevents the putrefaction of urine. Urine thus treated became turbid after 18 days, but still gave the reactions of fresh urine and did not show a trace of alkalescence.

C. S.

* 30 lbs. of hops contain 0·547 lbs. of nitrogen; 120 lbs. of hop-returns, however, contain 0·766 lbs., *i.e.*, 0·219 lb. more than hop, which difference must be added to the nitrogen amount in barley.

† The above difference of 4·01 p. c. must partly be put down for the nitrogen in the smoothing-water, which by accident was not determined.

# PAPERS READ BEFORE THE CHEMICAL SOCIETY.

## XIII.—*On Aluminum Nitride, and the Action of Metallic Aluminum upon Sodium Carbonate at High Temperatures.*

By Prof. J. W. MALLET, University of Virginia.

WISHING to try whether aluminum can be made to take up carbon as iron does in the production of steel, I proposed to myself to heat very strongly a mixture of metallic aluminum (in excess) and an alkaline carbonate; it having been stated* that from these materials free carbon and an alkaline aluminate are produced. The result was negative so far as the formation of any well defined aluminum carbide was concerned, very little carbon apparently being taken up by the surplus metal, and that little mostly, if not altogether, in a state of mere admixture, and producing no marked effect on the physical properties of the metal. Incidentally, however, certain other results were obtained which are worth recording.

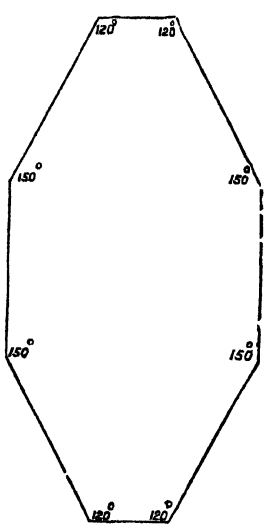
In the first place, although the reaction seems to begin as above stated, it goes further, and at a very high temperature the sodium is completely reduced, and volatilised so completely that the residue from the interior of the crucible, if examined with due care to avoid dust, handling, &c., actually fails to afford more than the faintest spectroscopic indication of the presence of the alkaline metal. At first the arrangement used was that of weighed pieces of aluminum ingot, of 10 or 15 grams each, imbedded in dry sodium carbonate, or aluminum filings mixed with the carbonate, contained in a crucible of Bunsen's hard carbon with a cover of the same, the whole placed in an outer plumbago crucible of good quality with plumbago cover, the inner crucible being enclosed on all sides by a thick layer of well-rammed lamp-black. A wind furnace of strong draught was used, with the hard carbon deposit from coal-gas retorts as the fuel. This material, whose employment was suggested by Violette,† when broken into pieces the size of a small egg, affords an extremely high temperature, the draught through grate and fuel

* Ch. and A. Tissier, *Comptes rendus de l'Académie des Sciences*, 29 Déc., 1856, p. 1187, as quoted by Ed. Uhlenhuth, Die Darstellung des Aluminiums, u.s.w. (The abstract in the *Comptes rendus* does not give all the details quoted.)

† *Comptes rendus de l'Académie des Sciences*, 28 Oct., 1872, p. 1028. I obtained a supply of 3 or 4 tons of this retort carbon from the Richmond gas works.

remaining unimpeded by ash or clinker, since the amount of mineral matter* present is very small and is separated during combustion in such a light, finely-divided state, that nearly all of it goes up the chimney. The fire was kept up for four or five hours with full intensity, and 24 hours afterwards the crucible on being taken out was too hot to be easily handled. The plumbago crucible was in great measure burned away and melted down upon the fire-brick used as a support, but was nowhere entirely pierced. The lamp-black was intact. The sodium disappearing from the residue, much of the aluminum was found oxidised, but as the reduction of the former metal might be attributed to the carbon of the crucible, while the oxidation of the latter might be due to carbon monoxide reaching it, the experiment was varied by enclosing the alkaline carbonate and aluminum in a *lime* crucible (with cover of the same), this being placed inside that of hard carbon, and the latter packed with lamp-black into a plumbago pot. The result was the same, the sodium disappearing completely, while an amount of aluminum somewhat more than equivalent to the oxygen of the carbonate used was found converted into alumina. The explanation of this excess, namely, the action of the metal upon carbon monoxide, was afterwards examined.

Beside a fused regulus of surplus metallic aluminum, the residue found in the crucible consisted in each case of a dark-grey, nearly black mass, sintered together and porous, the cavities of which were lined with lustrous little crystals of colourless alumina, hard enough to scratch topaz and chrysoberyl when rubbed on with the end of a rod of block tin.




These crystals were sometimes grouped, but for the most part independent hexagonal scales, occasionally thin enough to exhibit brilliant interference colours when examined with the microscope.

They were generally shortened in the direction of one lateral axis of the hexagonal prism, the two angles at whose extremities were replaced, thus giving the projection as figured; but several modifications were observed. A few thicker crystals were met with, showing lateral faces, both rhombohedral and prismatic.

The largest scales measured ·510 milli-

* The amount of ash and its composition have been examined by one of the students in the University of Virginia Laboratory, and the results will soon be published.

metre across on the major diameter, but most of them did not exceed ·025 mm.

Carbon was found in the residue in three different forms—viz.:

1. Much the larger part was black, opaque, pulverulent, altogether amorphous, and without lustre. Particles of this were sometimes caught in the little alumina crystals, and more or less symmetrically distributed in them.

2. In cavities of the crucible residue a few delicate locks of fine threads were found, appearing under the microscope as long, slender filaments with even surface, black, opaque, and lustrous, often singularly contorted. Some of these were as much as 6 or 7 mm. long, with a diameter of about ·013 mm. They burned completely away in oxygen, producing $CO_2$.

3. Other threads were occasionally found of less length and double or treble diameter, having the same general appearance under the microscope, except that the surface was mammillated, forming a succession of little knobs or protuberances. These often penetrated the crystalline scales of alumina at right angles to the principal surface, several of the little crystals occurring spitted upon the same carbon thread. The carbon left a scarcely visible trace of ash on combustion in oxygen.

These capillary forms of carbon are probably identical with those observed by Gay-Lussac* as deposited in porcelain furnaces with bad draught, and by Colquhoun and Braylay* as produced in the manufacture of steel by cementation in an atmosphere of coal-gas.

To determine whether carbon monoxide is decomposed by aluminum at high temperatures, a lump of the metal was exposed to the full heat of the furnace for several hours, in one instance in an otherwise empty hard carbon crucible, in a second experiment imbedded in loose, porous lime filling a similar crucible; in both cases lamp-black well rammed on the outside to a thickness of three-quarters of an inch ensured any carbon dioxide of the furnace atmosphere being reduced to monoxide in passing through. The aluminum was found covered with a hard, mammillated crust of carbon, like that from gas-retorts, ·2 to ·3 mm. thick, not easily detachable, and fully as difficult to burn in oxygen as diamond. The amount of carbon thus deposited was determined, and found to be far less than that obtained under the same conditions—quantity of materials, surface exposed, temperature, time, &c.—save that the metal was surrounded by sodium carbonate; leaving no doubt of the reduction of the latter by aluminum.

On the outside surface of the aluminum regulus obtained in all the above experiments, and projecting from the surface of cavities therein,

* Gmelin's *Handbook of Chemistry* (Cav. Soc. transl.), vol. ii, p. 84, quoting *Ann. Chim. Phys.*, vol. iv, p. 67, and *Ann. Phil.*, vol. xxviii, 1 and 192, &c.

some little crystalline particles of yellow colour were seen, and these were brought to light in large number, along with little yellow amorphous crusts, on dissolving the metal in well diluted hydrochloric acid. On examination, this yellow substance turned out to be aluminum nitride, a compound which has not, I believe, hitherto been produced and described. As most of it was found after solution of the metal mixed with a much larger quantity of alumina and carbon, it proved to be a matter of great difficulty to obtain enough of it in a reasonably pure state for analysis.

The nitride is of pale-yellow colour when amorphous, bright honey-yellow and translucent when crystallised. The crystals, though beautifully sharp and lustrous, were very minute—the largest not more than ·2 mm. in diameter—and so grouped together as to make it almost impossible to get such projections under the microscope as would permit plane angles to be measured. The general aspect was that of short rhombic prisms with dihedral summits, the end faces inclined on the lateral edges at angles not far from 120°.

The little particles were brittle, and not hard enough to scratch glass. Enough could not be collected free from foreign matter to determine the specific gravity. On exposure to damp air at common temperatures, the crystalline nitride gradually becomes sulphur-yellow and opaque, and in the course of a week or two crumbles down into white, pulverulent alumina, giving off ammonia. The amorphous nitride undergoes the same change, but in less time. Water, hot or cold, seems to have no immediate effect. Acids and caustic alkalies in solution attack it, rapidly if concentrated, slowly if dilute—an ammonium salt or free ammonia being produced, and the aluminum dissolved at the same time. When it is fused with potassium or sodium hydrate, ammonia is readily given off, and an alkaline aluminate formed. Heated alone in the air, the nitride slowly changes to dingy-grey, and is converted into alumina, but after two hours' roasting at a red-heat the residue still gave off ammonia on fusion with caustic alkali. Treatment with chlorine-gas, and with sodium thiosulphate, both failed to give any evidence of the presence of a cyanide.

Selecting the cleanest portions of aluminum regulus, dissolving out most of the metal with very dilute hydrochloric acid, but stopping the action before the steady evolution of hydrogen had ceased, and then carefully picking out under a lens the little crystalline grains of nitride, I succeeded with much trouble in collecting but ·0374 gram (quickly dried at 120° C.) in a state of nearly perfect purity. This small quantity was fused at a gentle heat with sodium hydrate in a little silver crucible placed in a tube of hard glass; the ammonia formed was swept out by a current of pure hydrogen, collected in hydrochloric acid, and determined as chloroplatinate. The contents of the crucible,

dissolved out with hydrochloric acid, left a minute residue of hard crystalline alumina, and from the solution the aluminum of the nitride was determined.

The results were—

| | | Per cent. |
|---|---|---|
| Aluminum ..... | ·0243 | 65·0 |
| Nitrogen ..... | ·0115 | 30·7 |
| Alumina (cryst.) ..... | ·0008 | 2·1 |
| | ·0366 | 97·8 |

2·132 grams of the *crude* residue from action of dilute hydrochloric acid on the aluminum regulus, taken in fine powder, was boiled with moderately strong solution of sodium hydrate, the ammonia given off collected, the solution cooled, diluted, and filtered, the filtrate acidified and evaporated to dryness to remove a little silica,* and on re-solution the aluminum (assumed as that of the nitride) determined.

The portion undissolved by sodium hydrate was dried at 120° C., weighed, and strongly heated in oxygen to burn off carbon; it left nothing but crystalline alumina with a little ferric and cupric oxides* and traces of combined silica.*

The results were—

| | | Per cent. |
|---|---|---|
| Aluminum (dissolved) ..... | ·239 | 11·21 |
| Nitrogen ..... | ·111 | 5·21 |
| Dissolved silica ..... | ·018 | ·85 |
| Crystalline alumina ..... | 1·504 | 70·54 |
| Carbon..... | ·249 | 11·68 |
| | 2·121 | 99·49 |

From the above figures we may fairly deduce the formula $Al_2N_2$, since, throwing out all mechanically mixed substances and loss, and looking only to the ratio between aluminum (of the nitride) and nitrogen, we have—

| | Found. | | Calculated. |
|---|---|---|---|
| | No. 1. | No. 2. | |
| Aluminum ..... | 67·9 | 68·27 | 66·18 |
| Nitrogen ..... | 32·1 | 31·73 | 33·82 |
| | 100·0 | 100·00 | 100·00 |

An excess of aluminum was to be expected, as some crystalline alumina must have been taken up by the sodium hydrate.

The quantity of the nitride formed in each experiment was small,

* Impurities of the original ingot of metallic aluminum.

but varied a good deal, apparently in consequence of the temperature required being very high, and more or less early closing the pores of the plumbago crucible by partial fusion, so that nitrogen from the furnace atmosphere no longer passed through. When aluminum alone was heated, no sodium carbonate being used, but very few yellow specks of nitride were visible, yet on exposure to moist air in a closed bottle the whole surface in time became covered with a white powder of alumina, and a piece of reddened litmus paper suspended to the stopper became blue.

## XIV.—*On the Volatility of Barium, Strontium, and Calcium.*

By Prof. J. W. Mallet, University of Virginia.

In some experiments on the action of metallic aluminum upon sodium carbonate at very high temperatures, I used a lime crucible inside one of hard carbon, and, finding the lime partially sintered together (from the formation of calcium aluminate) and easily removable with scarcely any mechanical loss, I weighed it as well as the residue it enclosed. The result of the weighing, after considering the oxidation of aluminum, separation of carbon, &c., at once suggested the idea that an appreciable quantity of calcium must have been reduced and volatilised. This idea has been confirmed by further and more careful examination, and the same fact observed in reference to barium and strontium.

The two following forms of experiment were used:—

(*a.*) A solid piece of ingot aluminum weighing 10—20 grams was placed in the middle of 20—25 grams of dry sodium carbonate enclosed in a little cornet of tissue paper (weighing but about 0·3 gram) and embedded in 30—40 grams of lime freshly prepared from fine white marble. This was contained in a crucible of Bunsen's hard carbon, with well fitted cover of the same, which was placed in an outer plumbago crucible, the intervening space being packed with well rammed lamp-black, and a plumbago ware cover placed over all.

(*b.*) The same arrangement was repeated, except that the sodium carbonate and paper cornet were omitted, and the aluminum—either in three or four embedded pieces or in admixed filings—was in direct contact with the lime.

Baryta and strontia were similarly treated; only one experiment being made with strontia, and that in form (*a*).

The extremely high temperature of the wind furnace used was derived from the combustion of the hard carbon deposit from coal-gas retorts, and was maintained for several—usually five or six—hours.

The evidence of the reduction and volatilisation of the metals in question falls under three heads—

1. The absolute disappearance of a portion of the calcium, barium, or strontium placed in the crucible as oxide when the residue after heating was carefully examined. The examination extended to four separate portions of the crucible contents, namely, the more or less metallic nucleus of the aluminum left in the centre, the remains of the surrounding alkaline earth,* the whole of the hard carbon crucible and cover crushed and pulverised, and the whole of the lamp-black from between this and the plumbago crucible.† The first generally afforded a very little of the calcium, &c., partly as aluminate and partly as oxide mechanically entangled on the surface; the second reproduced the greater part of that used; the third yielded no inconsiderable amount, absorbed as aluminate into the pores of the hard carbon; and in the fourth the barest traces were discoverable.

These materials were first exhausted by heating with strong hydrochloric acid; the crucible and lamp-black were burned to ash, and what remained of each was then thoroughly broken up by fusion with sodium hydrate, &c., taking care to remove a little silica completely by hydrofluoric acid. Although the lime, baryta, and strontia used were very nearly pure, anhydrous, and free from carbonate, the real amount of metal in each was determined as oxalate and sulphate respectively in a separate sample.

In every experiment there was loss to a weighable extent of the metal of the alkaline earth. The precise numerical results are, of course, not very important, as the intensity of furnace temperature, and the time it lasted, were not accurately measurable, but the following figures are quoted:—

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 32·171 | grm. | of | (real) | CaO | taken | lost | (*a*) — | ·803 | grm. | = 2·49 p. c. |
| 36·246 | ,, | ,, | ,, | ,, | ,, | ,, | (*a*) — | 1·139 | ,, | = 3·15 ,, |
| 34·710 | ,, | ,, | ,, | ,, | ,, | ,, | (*b*) — | ·765 | ,, | = 2·24 ,, |
| 33·847 | ,, | ,, | ,, | ,, | ,, | ,, | (*b*) — | ·782 | ,, | = 2·31 ,, |
| 42·321 | ,, | ,, | BaO | ,, | ,, | ,, | (*a*) — | ·834 | ,, | = 1·97 ,, |
| 45·444 | ,, | ,, | ,, | ,, | ,, | ,, | (*b*) — | ·799 | ,, | = 1·76 ,, |
| 39·087 | ,, | ,, | SrO | ,, | ,, | ,, | (*a*) — | ·891 | ,, | = 2·28 ,, |

* These two portions were merged into one when aluminum *filings mixed* with the oxide were used.

† A trifling quantity of lime occurring in the ash of the carbon crucible and lamp-black, was by separate experiments determined and allowed for.

2. In these experiments the aluminum could take up oxygen only from the sodium carbonate, from the lime, &c., and from carbon monoxide penetrating the crucible and lamp-black. When no alkaline carbonate was used, the quantity of metallic aluminum left in the residue, as determined by the amount of hydrogen evolved on solution,* seemed to show that oxidation took place to a decidedly greater extent when lime or baryta was present than when the metal was heated *by itself* in the hard carbon crucible (obtaining oxygen only from CO); and when sodium carbonate was also employed, the oxidation exceeded that referable to the whole of the oxygen in this salt, plus the amount which I had been led by the last named experiment to attribute to carbon monoxide.† This goes to show that the lime, baryta, &c., are not volatilised as oxides, but after reduction to the metallic state, which conclusion is, independently, much more likely than the reverse.

3. By observing at short intervals with the spectroscope the light carbon monoxide flame of the furnace during the heating of the crucibles, the characteristic lines of the metals volatilised were, in the later stages of the heating, distinctly seen, though with some difficulty, on account of the glare of light from the fuel and the furnace walls. I should not lay much stress upon this in reference to calcium, although it did not appear in an examination made of the ash of the retort carbon fuel by one of my laboratory students, but the barium and strontium spectra are far less likely to have been derived from any extraneous source. The lines were seen only when the furnace was at a very high temperature. They seemed to be more distinct when sodium carbonate was used than in its absence, and the losses of weight experienced seem to confirm the supposition that under the former condition volatilisation occurred to greater extent, but of this I do not feel quite sure.

If it be so, it is in accord with the view lately expressed in another paper, that reduction of sodium carbonate by aluminum takes place by two stages;—1st, separation of carbon and formation of sodium aluminate; and, 2nd, reduction of the latter by more aluminum,—this second change occurring at a much higher temperature than the former. The bearing of this question, as to *sodium vapour* reducing lime and baryta at a very high temperature, upon Davy's‡ supposed

* Checked as to impurities in the metal used by a similar comparative experiment with a piece of the same ingot which had not been heated.

† The extent to which carbon monoxide penetrated the crucible must have varied much during the heating, as the porosity of the crucible was altered by incipient fusion. It is remarkable, the experiments being carried on under no materially increased pressure, that in each case, but especially when baryta was used, the residue of alkaline earth contained a very appreciable amount of carbonate, as also of cyanide.

‡ Sir H. Davy "*Elements of Chemical Philosophy*," and Bakerian Lecture for 1809.

reduction vapour of the same by potassium (at probably a much lower temperature), is not without interest. The accuracy of his results has been doubted, though they have never, I believe, been directly refuted by more recent experiment. Matthiessen's remarks* as to the incapability of potassium and sodium to decompose calcium chloride are not inconsistent with the idea of reduction at temperatures high enough to volatilise both the alkaline chloride or oxide formed and the metal reduced. In my experiments, however, I have no doubt that the aluminum was at any rate the chief reducing agent.

The above results are not altogether surprising, in view of the well known wasting away of lime points in the oxyhydrogen flame, the production of spectra of barium, strontium, and calcium from the oxides in a good ordinary blowpipe flame, &c. They connect themselves in an interesting way with the occurrence of the lines of the metals in question in the solar, and in part in stellar spectra.

The extent to which volatilisation can be carried in close vessels is, however, remarkable, and must modify the views generally entertained of a radical difference in this respect between the metals of the alkalies and those of the alkaline earths. As between the members of the latter group, calcium would seem from these results to be the most volatile, and barium the least, the reverse of what I should from analogy have expected, though inability to measure, or even closely estimate, such high temperatures as have been used in the above experiments makes this largely matter of conjecture.

## XV.—*The Simultaneous Action of Iodine and Aluminium upon Ether and Compound Ethers.*

By J. H. Gladstone, Ph.D., F.R.S., Fullerian Professor of Chemistry in the Royal Institution, and Alfred Tribe, Lecturer on Chemistry in Dulwich College.

It is well known that aluminium has no action upon either water or alcohol; but in previous communications to this Society we have shown that in presence of aluminic bromide or iodide, an action immediately takes place, with production of alumina and hydrogen in the case of water, and of aluminic ethylate and hydrogen in the case of alcohol. This led us to expect that if ether were exposed to the action of the same agents, it might give us either ethyl and aluminic

* Quoted in Watts's "*Dictionary of Chemistry*," vol. i, p. 715.

oxide, or ethyl and aluminic ethylate; and perhaps throw some light on the nature of the chemical change.

Upon trying the experiment, we found that ether remained unaffected, even when boiled with aluminium and aluminic iodide, but that an oily body formed when it was exposed to the simultaneous action of iodine and aluminium.

This reaction was investigated, and the following experiment illustrates the general course pursued and the results obtained:—

27 grams of iodine with 2 grams of finely cut aluminium foil, that is, rather more than an equivalent quantity of aluminium, were mixed in a flask, and 20 c.c. of pure ether were added. A sensible rise of temperature took place at once, and in a minute or so the ether boiled violently, and was prevented from escaping only by an inverted condenser to which the flask was attached. This continued for about five minutes, when the action gradually ceased. The flask was now connected with an ordinary condenser and heated by immersion in boiling water, when a slightly brown ethereal liquid distilled, from which, by agitation with water, 3·5 c.c. of a body containing iodine and heavier than water separated. A brown semi-solid residue was left in the flask, and this was now slowly heated to 150° C. by immersion in a paraffin-bath, when again an oily body containing iodine distilled, which, after shaking with water, measured 6·5 c.c. On heating to a still higher temperature (200°), the residue frothed somewhat, and ·5 c.c. more of the oily body was obtained, making a total of 10·5 c.c.

The different portions of the oily body were added together, washed, dried, and subsequently distilled. It began to boil at 55°, and quickly rose to 70°, between which and 72° the greater part passed over. This portion resembled ethyl iodide in odour, had the same boiling point, and a specific gravity of 1·884 at 17° C., which agrees fairly with the known specific gravity of that body. When 5 c.c. (9·4 grams) were added to a copper-zinc couple wet with water, 1191 c.c. of gas burning with a luminous flame were obtained at the ordinary temperature in 28 hours. Assuming the body to be pure ethyl iodide, it should have yielded, under the circumstances, and according to our previous work, 1249 c.c. of ethyl hydride.

The residue left in the flask, after heating for some time at 200°, was light brown in colour, and weighed 14·59 grams. It dissolved almost completely in alcohol and water. On heating the entire residue from another experiment, over a lamp, 200 c.c. of gas were obtained, of which 68·2 were absorbable by bromine, the remainder burning with a slightly luminous flame, and a residue was left in the flask which consisted of alumina with some iodine.

The formation of the ethyl iodide might be accounted for on the supposition—1. That the products are ethyl iodide and aluminic oxide.

2. That the products are ethyl iodide and aluminic oxyiodide or its elements. 3. That they are ethyl iodide and aluminic iodoethylate, or its elements. If the first of these were true, the residue, after distilling off the ethyl iodide would consist of alumina and be insoluble in water and alcohol, but as it is soluble in these menstrua, this supposition is negatived. If the second were true, the residue, consisting of oxyiodide, could certainly not have yielded hydrocarbons by heat. The inference is therefore, that the third supposition is in the main correct, but, as a somewhat greater quantity of ethyl iodide is produced than even this requires, the probability is that the iodoethylate slowly splits up into alumina and ethyl iodide under the influence of heat—a conclusion confirmed by the amounts of iodine and alumina in the 14·59 grams of residue mentioned above. The quantities of these substances found were—

| | |
|---|---|
| Iodine ..... | 8·769 |
| Alumina ..... | 3·866 |

If the iodine be calculated as aluminic iodoethylate, 13·135 grams of the residue are accounted for, which would be equivalent to 2·365 grams of alumina, leaving, therefore, 1·501 which, added to 13·135 equals 14·636. The close agreement of this number with the weight of the residue confirms the belief that it consists of aluminic iodoethylate with alumina, and leaves but little doubt as to the truth of the third supposition.

*Aluminic Iodo-ethylate.*

As we know nothing more about the properties of this body than what has been gathered from the study of the fixed product of the aluminium iodine and ether reaction, we sought for a process by which it could be prepared in a state of purity. As we had already suspected its presence in the reaction with alcohol (previously described by us), and as the proportions expressed in the equation—

$$6(C_2H_5O.H) + Al_2I_6 + Al_2 = 2Al_2\left\{\begin{matrix}(C_2H_5O)_3\\ I_3\end{matrix}\right. + H_6,$$

appeared likely to give the iodo-ethylate, the following experiment was made:—

29 c.c. of alcohol containing 8·294 grams of aluminic iodide in solution were added to 0·556 gram of finely-cut aluminium foil, the inorganic constituents being in the proportions required by the above equation. The flask containing the materials was heated by immersion in boiling water, when hydrogen was at once evolved, and this continued for 15 minutes, 688 c.c. of gas being collected, that is, 7 c.c. above the calculated amount.

The product of the action left in the flask, which can consist of none other than aluminic iodo-ethylate or its elements mixed with or

in combination with alcohol, was a liquid of a brown colour and perfectly miscible with water, and on evaporation *in vacuo* it dried up to a non-crystalline semi-solid mass.

The whole of the non-gaseous product of an experiment similar to the above was heated in a distilling apparatus by immersion in boiling water. It gave off alcohol and a little ethyl iodide, leaving a non-crystallised brown mass. When this was heated between 100° and 200°, a little more alcohol passed over accompanied by a greater quantity (3 c.c.) of ethyl iodide, leaving alumina with a small quantity of iodine in the flask, which clearly indicates that the iodo-compound splits up, in presence of alcohol, into alumina and ethyl iodide at a high temperature.

The fact of this splitting up of the iodo-ethylate on distilling and heating with alcohol led us to expect that the residue from the iodine ether reaction, after heating to 200°, would also yield ethyl iodide on heating with alcohol. Such was found to be the case. It at the same time led us to expect that the whole of the iodine employed could, by the assistance of alcohol, be converted into ethyl iodide, which is practically shown to obtain by the following experiment:—

The product from 27 grams iodine, 2 grams aluminium, and 20 c.c. ether gave, on distilling at 100° C., 3·75 c.c. of ethyl iodide. 20 c.c. of absolute alcohol were now added, which occasioned a considerable evolution of heat, sufficient to drive over 1·75 c.c. of ethyl iodide. On heating first to 100° and then to 200°, in addition to alcohol, 9·5 c.c. of ethyl iodide passed over, making a total of 15 c.c., the theoretical quantity being 17·3 c.c. The residue left in the flask was almost white alumina, containing 1·4 gram of iodine.

Taking the whole of the facts above detailed into consideration, the simultaneous action of iodine and aluminium upon ether may be thus represented:—

$$3\left\{\begin{matrix}C_2H_5O\\C_2H_5\end{matrix}\right. + Al_2 + I_6 = Al_2\left\{\begin{matrix}(C_2H_5O)_3\\I_3\end{matrix}\right. + 3C_2H_5I.$$

This action of heat upon the aluminic iodo-ethylate when associated with alcohol, may be represented thus:—

$$Al_2\left\{\begin{matrix}(C_2H_5O)_3\\I_3\end{matrix}\right. = Al_2O_3 + 3C_2H_5I,$$

but it is probably the product of two actions, thus:—

$$(1)\ Al_2\left\{\begin{matrix}3C_2H_5O\\I_3\end{matrix}\right. + 3\left\{\begin{matrix}C_2H_5O\\H\end{matrix}\right. = 3C_2H_5I + Al_2\left\{\begin{matrix}3C_2H_5O\\(HO)_3\end{matrix}\right.$$

$$(2)\ Al_2\left\{\begin{matrix}(C_2H_5O)_3\\(HO)_3\end{matrix}\right. = Al_2O_3 + 3\left\{\begin{matrix}C_2H_5O\\H\end{matrix}\right..$$

It might be anticipated that iodine and aluminium, if allowed to act simultaneously upon other ethers than the ethylic, would yield their

corresponding iodides. Such the following experiment shows to be the case with amylic ether.

20 c.c. of this compound were added to a flask containing 2 grams of finely-cut aluminium foil, and 27 grams of iodine. There was no action apparent in 30 minutes, but soon afterwards the temperature was found to have risen sensibly, this quickly increased, and the action finished in 15 minutes.

The brown liquid left in the flask was heated by immersion in a paraffin-bath, slowly from the melting point of that substance, to 200° C. The distillate obtained after washing with water gave 15 c.c. of an oily body containing iodine.

It also appeared of interest to ascertain whether the reaction described is a general one with bodies containing $C_nH_{2n+1}$ radicals, or is applicable only to simple ethers. Experiments were accordingly made with the acetates of ethyl and amyl.

In one experiment with amyl acetate, 16·5 c.c. of this body were placed together with 13·9 grams of iodine and 1 gram of aluminium. The contents of the flask quickly rose in temperature, and the action became very energetic; it was over in 30 minutes. The flask was now slowly heated by a paraffin-bath to 200°, when an oily body containing iodine distilled, commencing at about 140°, and after agitation with water it measured 12 c.c. On drying with calcium chloride the greater part passed over between 137°—142°, and it had a sp. gr. of 1·44 at 11° C. As the boiling point of amyl iodide is said to be 146° and its sp. gr. 1·511, this product probably contained a little undecomposed acetate.

In an experiment with the ethyl compound, 9·3 c.c. of it were mixed with the same quantities of iodine and aluminium as in the previous experiment. The action was extremely violent, being nearly over in five minutes, and necessitating constant agitation of the flask in cold water. The flask was afterwards heated to 100° for thirty minutes to destroy the last traces of aluminium, and the temperature was then slowly raised to 200° C. An oily iodide distilled which, after washing with water, measured 7 c.c. On drying with calcium chloride and distilling, the whole boiled between 70°—72°, had a sp. gr. 1·98 at 9° C., and possessed the odour of ethyl iodide, with which it accords perfectly in boiling point and specific gravity. The theoretical quantity of ethyl iodide obtainable is 7·2 c.c.

The residues of both experiments consisted of aluminic acetate with a little iodide.

It is therefore evident that the metal in these reactions combines with the $C_2H_3O_2$ of the acetate, just as it does with the $C_nH_{2n+1}.O$ of the ethers, while the $C_nH_{2n+1}$ immediately enters into union with iodine forming the iodide, thus:—

$$6\left\{\begin{matrix}C_nH_{2n+1}\\C_2H_3O_2\end{matrix}\right. + Al_2 + I_6 = 6\left\{\begin{matrix}C_nH_{2n+1}\\I\end{matrix}\right. + Al_2(C_2H_3O_2)_6.$$

This last research has placed us in a position to form a more definite opinion as to the manner in which the peculiar chemical change recently described by us, is brought about. Water, alcohols, and ethers are well known to be analogous bodies, and each may be considered as binary compounds in which the radical H or $C_nH_{2n+1}$. is united to the oxygen compounds of a similar radical, thus:—

| | |
|---|---|
| Water ..... | $H.HO$ |
| Alcohols..... | $H.C_nH_{2n+1}.O$ |
| Ethers ..... | $C_nH_{2n+1}.C_nH_{2n+1}O$. |

Now aluminium shows a great tendency to combine with hydroxyl. We know, for instance, that an aqueous solution of acetate of aluminium will form the hydrate $Al_2(HO)_6$, and give acetic acid by boiling or diffusion; and the iodide, bromide, or chloride of aluminium exposed to damp air gives off free acid. Similarly, we believe, the aluminium is ready to combine with $C_nH_{2n+1}O$, if a halogen be present to remove the H or $C_nH_{2n+1}$.

Our present belief is that the chemical change takes place through the intervention of intermediate bodies, thus:—

$$(a.)\ Al_2I_6 + 3H_2O = Al_2\left(\begin{matrix}HO\\I_3\end{matrix}\right)_3 + 3HI.$$

$$(b.)\ Al_2\left(\begin{matrix}HO_3\\I_3\end{matrix}\right. + 3H_2O = Al_2(HO)_6 + 3HI.$$

$$(c.)\ 6HI + Al_2 = Al_2I_6 + 3H_2.$$

It will be understood that the complete hydration of the aluminium iodide, as by equation *b*, occurs only when the excess of hydriodic acid is destroyed, as by equation *c*, and thus the evolution of hydrogen will be continuous as long as aluminium and water are present, which accords with our experiments.

We find, moreover, that an aluminic iodo-hydrate corresponding with $Al_2\left(\begin{matrix}HO\\I_3\end{matrix}\right)_3$ in composition readily dissolves in water, and when heated with aluminium gives an equivalent amount of hydrogen. We find also that an alcoholic solution of its carbo-hydrogen analogue also yields equivalent quantities of hydrogen when heated with aluminium. This tends to confirm the explanation above given, and also elucidates the decomposition of alcohol by the joint action of aluminium and its iodide, which may be represented in a similar way to the above, substituting the radical $C_2H_5O$ for HO.

The reaction with ether is analogous to what occurs with water or alcohol according to equation (*a*), the elements being free, thus:—

$$Al_2 + I_6 + 3(C_2H_5.C_2H_5O) = Al_2\left\{\begin{matrix}(C_2H_5O)_3\\I_3\end{matrix}\right. + 3C_2H_5I.$$

# XVI.—COMMUNICATIONS FROM THE PATHOLOGICAL LABORATORY OF DR. THUDICHUM.

## No. V.—*Note on some Trials of Frankland and Armstrong's Combustion Process* in vacuo.

By J. L. W. Thudichum and C. T. Kingzett.

When Frankland and Armstrong (*Chem. Soc. Journ.*, xxi (1868), 89) described their process of combustion *in vacuo* as a means of estimating organic carbon and nitrogen contained in water-residues, they incidentally expressed their belief that it would be found generally useful in the analysis of all organic compounds containing nitrogen, which are not volatile at ordinary temperatures. With the exception of a few determinations of carbon and nitrogen in residues from the evaporation of solutions containing known quantities of urea and hippuric acid, together with sodic carbonate, they gave no analyses to support this anticipation, and we are not aware of any experiments made by others to test its correctness. From its nature the process seemed particularly adapted to the exigencies of physiological and pathological researches, where the quantities of material at the disposal of the investigator are not rarely so small as to exclude the possibility of determining the elements by the ordinary processes of analysis, or of verifying the results of a single analysis by repetition. In order to test this surmise we have made the following experiments, which, although small in number, seem to be sufficiently precise to serve as materials for the formation of some definite conclusions on the subject.

Relating to the materials to be employed in the analysis, Frankland and Armstrong state (*loc. cit.*, p. 93) that cupric oxide prepared from the nitrate should on no account be used, since, even after being actually fused, it evolves considerable quantities both of carbonic anhydride and nitrogen when ignited *in vacuo*. Our experience has in a measure corroborated this statement, so far as relates to carbonic anhydride (or rather gas absorbed by caustic potash), but not as regards nitrogen. This is shown by the following experiments:—

*Exp.* I. A tube of the usual size was charged with cupric oxide made from the nitrate, and of the same kind as that which we employ in our ordinary combustions, with a roll of metallic copper in front. This was rendered vacuous, heated to bright redness, and the pump set working and maintained so for about half an hour. By the time the second vacuum was obtained there was collected 1·5 c.c. gas,

which, after the ordinary corrections, became 1·0 c.c. normal. It was almost entirely absorbed by potash.

*Exp.* II. In this experiment the procedure was identical with that described under experiment I, except that, after the tube had been rendered vacuous and heated to redness, the pump was not set working till the fire had been put out. In this way the cupric oxide gave off gas which when normal measured 0·5 c.c. On the introduction of some potash only a trace of gas remained unabsorbed. These experiments prove therefore that while the error involved in the use of cupric oxide as ordinarily prepared for combustion is great enough to destroy the accuracy of the determination of carbon, it does not seriously affect that of the nitrogen. But they also show that the error in the carbon is dependent upon variations in the vacuum in this manner, that it becomes less (by one-half in the above experiment) if the vacuum be not actively maintained at the time that the combustion-tube is at its highest temperature; or the experiments seem to indicate that cupric oxide retains carbonic anhydride at temperatures below glowing heat even in a vacuum, while the same cupric oxide does not retain it in a vacuum at bright red heat. This recalls the relations of hydrogen to metallic copper *in vacuo*, under ordinary pressure, which has been treated of before this Society on a former occasion. We incline to the belief that the small amount of carbon found in cupric oxide by the vacuum method is introduced, during the heating of the oxide, by diffusion of the products of combustion into the covered crucibles. The error may be entirely avoided, either by the precaution adopted by Frankland and Armstrong of using cupric oxide prepared from metal by oxidation in air, or by using cupric oxide heated to redness in a glass tube in which the vacuum has been actively maintained during the entire period of ignition.

We here take note of the fact that Frankland no longer uses plumbic chromate in the combustion of water-residues, as originally recommended by him and Armstrong, but conducts the entire operation with cupric oxide only.

*Exp.* III. In this experiment a combustion was made with the oxide of copper which had been used in experiment I, that is, which had given up *in vacuo* at a red heat its occluded carbon as carbonic anhydride. With it there was burned 0·0242 grm. of hematine, which by combustion with $PbCrO_4$ had furnished 61·81 per cent. C. In the present combustion it gave 28·1 c.c. $CO_2$, and 1·7 c.c. N, both normal, equal to 62·25 per cent. C. and 8·78 per cent. N, or a relation of N : C = 1 : 8·2. From a number of ordinary elementary analyses we had fixed the formula of this hematine as $C_{32}H_{32}FeN_4O_6$, in which the nitrogen stands to the carbon as 1 : 8, and which requires 61·53 per cent. C and 8·97 per cent. N.

We next made combustions *in vacuo*, with similar precautions, of the following substances:—

*Exp.* IV. Uric acid. 0·0845 grm. gave 57·7 c.c. $CO_2$, and 22·3 N.

*Exp.* V. Urea. 0·0350 grm. gave 15·6 $CO_2$, and 13·2 c.c. N.

*Exp.* VI. Leucine. 0·0408 grm. gave 41·3 c.c. $CO_2$, and 3·6 c.c. N.

*Exp.* VII. Bromobiliverdin. 0·0282 grm. gave 22·4 c.c. $CO_2$, and 1·38 c.c. N, = 6·12 per cent. N.

*Exp.* VIII. Bilirubin. 0·0483 grm. gave 9·96 per cent. N.

*Exp.* IX. $(Choline, HCl)_2PtCl_4$. 0·0536 grm. gave 4·20 per cent. N.

*Exp.* X. Myeline (from blood corpuscles). 0·0246 grm. gave 2·54 per cent. N.

If we consider these experiments as tests simply of the composition of substances which have not been specially prepared as test objects, although the composition of some was known from previous analysis, while others had been prepared according to the best rules and answered the current tests of purity, they are not very satisfactory. The carbon varies in a manner so as to be either deficient or in excess.

*Table showing Atoms of Carbon found if* N = 1.

| Substance. | Formula. | Atoms of Carbon. |
|---|---|---|
| Hematine ..... | $C_{32}H_{32}FeN_4O_6$ ..... | 8·2 |
| Uric acid ..... | $C_5H_4N_4O_3$ ..... | 1·27 |
| Urea ..... | $CH_4N_2O$..... | 0·561 |
| Leucine..... | $C_6H_{13}NO_2$ ..... | 5·7 |
| Bromobiliverdin. | $C_8H_8BrNO_2$ ..... | 8·1 |
| Bilirubin ..... | $C_9H_9NO_2$ ..... | 8·4 |
| Choline, $PtCl_4$ .. | $(C_5H_{13}NO.HCl)_2PtCl_4$.. | 5·7 |
| Myeline ..... | $C_{72}H_{164}N_3P_2O_{14}(CdCl_2)_2$.. | 26·0 |

The actual percentage of carbon in organic substances of a composition controllable by the atomic theory seems at present better determinable by combustion in the ordinary way. For many substances this may be explained at once by the well-known difficulty of burning carbon entirely without the aid of gaseous oxygen. The carbon determination seems, however, the least important part of the process and can be made useful, its faults notwithstanding, as an approximative measure of the proportion between carbon and nitrogen. For as the vacuum-method cannot be used for determining the hydrogen, a combustion must be made in the ordinary way in order to determine the percentage of this element, when a trustworthy carbon determination can always be effected simultaneously.

Considered only as a method for determining the quantity of nitrogen in any organic substance, the vacuum process seems excellent, and less

troublesome than the ordinary process in which air is displaced by $CO_2$. This is evident from the comparison of the results of some of the analyses already given with the relative numbers required by theory.

| | N per cent. | |
|---|---|---|
| | Theory. | Found. |
| Hematine, Exp. III ..... | 8·97 | 8·78 |
| Uric acid, Exp. IV ..... | 33·33 | 33·06 |
| Urea, Exp. V..... | 46·66 | 47·18 |
| Leucine, Exp. VI..... | 10·68 | 11·03 |
| Bromobiliverdin, Exp. VII.. | 6·08 | 6·12 |
| Bilirubin, Exp. VIII ..... | 8·58 | 9·06 |
| Choline plat. chl., Exp. IX.. | 4·52 | 4·20 |
| Myeline, Exp. X ..... | 2·24 | 2·54 |

If, however, the experimentalist will take the trouble of combining the vacuum method with the displacement method in which bichromate of potash and carbonate of soda is employed as the source of $CO_2$ (Thudichum and Wanklyn, *Chem. Soc. Journ.*, xxii [1869], 293), and if he will subject his caustic potash and mercury to the vacuum for some time, we believe that nitrogen analyses can be made which will surpass all others in accuracy, and in which not even that obstinate bubble in the gas-tube will be perceived which has puzzled so many of the best experimentalists.

The following examples are illustrative of the value of this combustion method as a test for the presence of nitrogen:—

*Exp.* XI was conducted with a body obtained in the chemolysis of myeline, which itself contains N. 0·0238 grm. gave 33·1 c.c. normal $CO_2$, and 0·39 c.c. normal N.

*Exp.* XII related to a similar substance. 0·0288 grm. gave 32 c.c. $CO_2$, and 0·3 c.c. N; both normal.

That is to say, both these substances contained, as was expected, traces of nitrogen, from non-completion of the chemolysis.

*Exp.* XIII was conducted on a red product from urine, termed urrhodine, and commonly believed to be identical with indigo-red.

0·0178 grm. gave 26· c.c. $CO_2$ normal, and 0·1 c.c. N normal, showing that the substance was non-nitrogenous, and therefore disproving the stated identity.

The vacuum-process seems also to admit of a new application for the determination of the nitrogen in some ammonium salts.

*Exp.* XIV. During an investigation, to which we need not more particularly refer here, there was obtained a volatile base, which was converted into sulphate, once recrystallised from boiling absolute alcohol and analysed.

0·0218, burnt as ordinarily *in vacuo*, gave 4·91 c.c. N normal = 21·23 per cent. nitrogen. Sulphate of ammonium $(NH_4)_2SO_4$ should contain 21·21 per cent. N. Further analysis showed the substance to be this salt.

*Exp.* XV. Ammonic chloride was now subjected to combustion *in vacuo*.

0·0210 grm. gave 4·5 c.c. N normal = to 26·80 per cent. N. Theory requires 26·16 per cent. N.

*Exp.* XVI. Next ammonic nitrate was burnt in the same way.

0·0190 grm. gave 5·38 c.c. N normal = to 35·42 per cent. N. Theory requires 35·00 per cent. N, if both atoms of N be given up, which proved, as is seen, to be the case.

These experiments indicate therefore a method of estimating nitrogen in ammonium salts, which possesses some decided advantages over the soda-lime process.

## XVII.—*On an Alkaloïd obtained from Jaborandi, its Platinic Compound, and their Formulæ.*

By Charles T. Kingzett.

In 1875 an alkaloïd was isolated from the leaves and stalks of jaborandi (*Pilocarpus pennatifolius*, of Lemaire), almost simultaneously and quite independently by Mr. A. W. Gerrard and M. Hardy. There is another kind of jaborandi, a species of Piper, from which Parodi has isolated an alkaloïd of the formula, $C_{20}H_{12}N_2O_6$.

To the alkaloïd upon which M. Gerrard worked, the name of pilocarpine has been given. He has detailed the methods of extraction, and states that it forms crystallisable salts with hydrochloric, nitric, and sulphuric acids. He further exhibited some crystals of the so-called hydrochloride in a dark brown mother-liquor, at the last meeting of the Pharmaceutical Conference, but neither at that time nor since has he, or M. Hardy, or any other observer, published any formulæ for the alkaloïd or its compounds. Mr. Gerrard has further stated his opinion that there are at least two alkaloïds in jaborandi, and that the one upon which he worked gave no precipitate with phosphomolybdic acid. Several other papers relating to this subject will be found in the *Year Book of Pharmacy*, for 1875.

More recently Hardy states that he has obtained from the distillate

of an aqueous extract of the leaves of jaborandi, a quantity of crude oil, containing a terpene which gave a crystalline di-hydrochloride. But the boiling point of 178° C., which he attributes to the hydrocarbon, would rather point to cymene than to a terpene. He also obtained a solid, colourless substance, which was not further examined (*L'Union Pharmaceutique*, vol. xvi, p. 365). My first experiment was conducted upon the leaves of the plant. These were thoroughly extracted with water of 70° C., and the extract concentrated to a small bulk, filtered from deposited matters, rendered acid by hydrochloric acid, and fully precipitated with phosphomolybdic acid. The bright yellow precipitate, after thorough washing, was decomposed after the method of Sonnenschein, that is by heating with excess of baryta, and the excess of barium was removed by carbonic acid. The filtrate was strongly alkaline, and was found to contain barium. This barium was carefully removed by sulphuric acid, and the filtrate, which gave the characteristic reactions of an alkaloïd with various reagents, was converted into hydrochloride, but all attempts to obtain crystals by concentration on a water-bath, or in a vacuum over sulphuric acid, or by spontaneous evaporation, proved vain.

In the next experiment I took the stems and twigs of jaborandi, and extracted them after they had been cut up into small fragments, with boiling water, until the last extract contained no appreciable quantity of matter.

The extract was distilled to a small bulk, and it was observed that the first few litres of distillate came over milky, and that on standing yellow oily drops deposited. The small quantity and its volatile nature defeated an attempt made to isolate it. The concentrated water-extract obtained as above was treated with an equal volume of strong alcohol, which threw down dark-coloured albuminous matter, &c. From the filtrate the whole of the alcohol was distilled off, and a great part of the water. The syrup of 300 c.c. was now extracted with much ether. Next ammonia was added, as Mr. Gerrard stated in a letter to me that he had found the alkaloïd in the water extract was combined with an acid, and the whole was again extracted with ether. Finally the syrup containing ammonia was extracted with chloroform.

The first ether extracts were strongly coloured; the after ones only faintly; the chloroform ones not at all. From all these extracts the solvents were distilled, and after many and various unsuccessful attempts to get the residues combined separately in a crystalline form with hydrochloric acid, no sign of crystallisation ever being obtained, all the products were united, ammonia added, and the whole again extracted by chloroform. The chloroform extracts on distillation left a coloured aqueous syrup, which was rendered strongly acid with nitric

acid, and gave a bulky yellow precipitate with phospho-molybdic acid. This precipitate was passed through the same treatment as that described above in the first experiment. The free base was found to contain barium, which was removed exactly by very dilute sulphuric acid, after which the whole was concentrated to a syrup of a pleasant nutty odour. The product was now acidified faintly with hydrochloric acid, and another attempt made to get a crystallisation, both by evaporation on a water-bath and *in vacuo*, &c., but as before, quite in vain.

I therefore now removed the hydrochloric acid by dilution with water and agitation with oxide of silver, and evaporated the filtrate to dryness, after digestion with charcoal, which removed much of the colour. The residue was dissolved in absolute alcohol, filtered from a trace of reduced silver, and again evaporated to dryness, and the drying completed in an air-pump over sulphuric acid during a fortnight. The product was now analysed, all combustions being effected in platinum boats, as the matter was soft and plastic, like gum.

(*a.*) 0 0204 grm. gave by combustion *in vacuo* with CuO and metallic copper, 21·8 c.c. $CO_2$, and 1·8 c.c. N. normal, showing the relation of the N : C to be 1 : 6.

(*b.*) 0·1872 grm. gave by combustion with $PbCrO_4$ and metallic copper, 0·3762 grm. $CO_2$, and 0·1404 grm. $H_2O$ = 54·80 per cent. carbon, and 8·33 per cent. hydrogen.

*Synopsis of Analyses.*

| | | | ÷ at. wgts. | ÷ N = 1. |
|---|---|---|---|---|
| | C | = 54·80 | 4·566 | 5·80 |
| | H | = 8·33 | 8·33 | 10·50 |
| Frankland's process | N | = 11·03 | ·787 | 1·0 |
| | O | = 25·84 | 1·615 | 2·0 |
| | | 100·00 | | |

After the above analysis was completed, the rest of the alkaloïd was dissolved in 87 per cent. alcohol. and treated with alcoholic platinic chloride, when a bulky precipitate was produced, but slightly soluble in cold, readily soluble in hot water. The yellow solution on concentration gave a crop of reddish-yellow octohedral crystals, which were isolated, rinsed with water, dried at 80° C., and analysed.

(*a.*) 0·0404 grm. gave by combustion *in vacuo* with CuO and Cu, 26·2 c.c. $CO_2$, and 2 3 c.c. N normal, giving as the relation of N : C 1 : 5·7, and the percentage of N = 7·12.

(*b.*) 0·3532 grm. gave with $PbCrO_4$ and metallic Cu 0·412 grm. $CO_2$, and 0·142 grm. $H_2O$ = 31·81 per cent. C., and 4·46 per cent. H.

(*c*.) 0·2120 grm. gave 0·0496 grm. platinum, and 0·2128 grm. AgI = 23·39 per cent. Pt, and 24·83 per cent. Cl.

*Synopsis of Analyses.*

| | | ÷ at. wgts. | ÷ Pt = 1. | |
|---|---|---|---|---|
| C = | 31·81 | 2·65 | 22·4 | |
| H = | 4·46 | 4·46 | 37·7 | |
| N = | 7·12 | ·508 | 4·3 | or |
| Pt = | 23·39 | ·118 | 1·0 | |
| Cl = | 24·83 | ·669 | 5·6 | |
| O = | 8·39 | ·524 | 4·4 | |

$C_{23}H_{35}N_4O_4.2HCl.PtCl_4$.

Now the analysis of the free alkaloïd led to $C_{5\cdot8}H_{10\cdot5}NO_2$. Multiplying this by 4, and deducting $4H_2O$, we obtain the above formula derived from the analyses of the platinum salt:—

$C_{23}H_{34}N_4O_4.(4H_2O)$ = as dried *in vacuo*.
$C_{23}H_{35}N_4O_4$ = as combined with $PtCl_4$.

In conclusion, I have to express my indebtedness to Dr. Thudichum for having kindly placed his laboratory at my disposal during the prosecution of the foregoing research.

# ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

## General and Physical Chemistry.

### On the Specific Rotatory Power of Substances in Solution.

By H. LANDOLT (Deut. Chem. Ges. Ber., ix, 901—914).

THE author has determined the rotatory power of several liquids when diluted with varying proportions of other liquids having no action on polarised light. His experiments have led to the following conclusions:—The specific rotatory power of an active substance undergoes a gradual change on diluting the substance more and more with an indifferent liquid, becoming greater or less according to the nature of the active substance. The rotatory power of oil of turpentine and ethyl tartrate is increased by dilution, whilst that of nicotine and camphor is diminished. Increasing quantities of different diluents produce very different amounts of change in the rotatory power of the same active substance.

The rotatory power of an active substance may be calculated from that of its solutions. The degree of accuracy with which the calculation can be made varies with each substance, and depends upon (1) the general extent of the alteration in the rotatory power of the solution produced by dilution; (2) the kind of change produced by increasing quantities of the diluent, *i.e.*, whether the change is one which can be represented graphically by a straight line or by a more or less curved line; and (3) the strength of the solution employed.

It follows, from the author's experiments, that in cases where the amount of rotation can be represented by the equation $[\alpha] = A + Bq$ (where $A$ and $B$ are constants, and $q$ the percentage of the diluent in the liquid examined), the constant $A$ coincides, within a few tenths of a degree, with the actual rotatory power of the pure substance, when $q$ does not exceed 50. But where the formula $[\alpha] = A + Bq + Cq_2$ becomes necessary, differences of more than one degree are observed whenever the solution contains less than 80 per cent. of the active substance.

The following formulæ have been calculated by the author from the results of his observations.

Oil of turpentine (lævorotatory)—

In alcohol .... $[\alpha]_D = 36{\cdot}974 + 0{\cdot}0048164\,q + 0{\cdot}0001331\,q^2$;
In benzene .... $[\alpha]_D = 36{\cdot}970 + 0{\cdot}021531\,q + 0{\cdot}000066727\,q^2$;
In acetic acid.. $[\alpha]_D = 36{\cdot}894 + 0{\cdot}024553\,q + 0{\cdot}00013689\,q^2$.

Oil of turpentine (dextrorotatory) in alcohol—

$$[\alpha]_D = 14{\cdot}173 + 0{\cdot}011782\,q.$$

Nicotine (lævorotatory)—

In alcohol $[\alpha]_D = 160{\cdot}83 - 0{\cdot}22236\ q$;
In water $[\alpha]_D = 115{\cdot}019 - 1{\cdot}70607\,q + \sqrt{2140{\cdot}8 - 108{\cdot}867 + 2{\cdot}5572q^2}$.

Ethyl tartrate (dextrorotatory)—

In alcohol. . . $[\alpha]_D = 8{\cdot}409 + 0{\cdot}018667\ q$;
In wood-spirit $[\alpha]_D = 8{\cdot}418 + 0{\cdot}062466\ q - 0{\cdot}00034786\ q^2$.
In water . . . . $[\alpha]_D = 8{\cdot}090 + 0{\cdot}20032\ q$.

In sufficiently strong solutions the constant $A$ is the same whatever solvent is employed. On calculating, by means of the foregoing formulæ, the specific rotatory power of a substance with increasing proportions of the diluent, the numbers become more and more divergent until at last $q = 100$, *i.e.*, the dilution becomes infinite. The total amount of change produced by solvents in the rotatory power of the active substances experimented on is shown in the following table, which gives the calculated values for the limits $q = 0$ and $q = 100$, preceded by the rotation produced by the pure substance as observed directly:—

| | $[\alpha]_D$ $q = 0$. | $[\alpha]_D$ $q = 100$. | Difference. |
|---|---|---|---|
| *Oil of Turpentine* (lævorotatory). | ° | ° | ° |
| Observed directly | 37·01 | — | — |
| Calculated from mixtures with alcohol | 36·97 | 38·79 | 1·82 |
| " " benzene | 36·97 | 39·79 | 2·82 |
| " " acetic acid | 36·89 | 40·72 | 3·83 |
| *Oil of Turpentine* (dextrorotatory). | | | |
| Observed directly | 14·15 | — | — |
| Calculated from mixtures with alcohol | 14·17 | 15·35 | 1·18 |
| *Nicotine* (lævorotatory). | | | |
| Observed directly | 161·55 | — | — |
| Calculated from mixtures with alcohol | 160·83 | 138·59 | 22·24 |
| " " water | 161·24 | 74·13 | 87·11 |
| *Ethyl Tartrate* (dextrorotatory). | | | |
| Observed directly | 8·31 | — | — |
| Calculated from mixtures with alcohol | 8·27 | 10·19 | 1·92 |
| " " wood-spirit | 8·42 | 11·19 | 2·77 |
| " " water | 8·09 | 28·12 | 20·03 |

Hence it appears that in comparing the rotatory powers of different substances, those numbers only are strictly applicable which pertain to the pure substances; and that numbers obtained by observations of solutions are the less trustworthy the more dilute the solutions. It being a matter of indifference what solvents are employed, those which yield the strongest solutions should be selected. Observations with

solutions containing only a small percentage of active substance are worthless.

J. R.

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**On the Specific Rotatory Power of Camphor.** By H. LANDOLT (Deut. Chem. Ges. Ber., ix, 914—917).

THE camphor employed in the author's experiments was purified by sublimation. It boiled at 204° and solidified at 175°. Its rotatory power was determined by dissolving it in various proportions of each of the undermentioned liquids and observing the rotation produced by the solutions at 20°. It was found that with all the solvents except the last two, the rotatory power of the camphor in solution could be expressed by the formula $[\alpha] = A - Bq$ ($A$ and $B$ being constants, and $q$ the percentage of solvent in the solution); that is to say, the alteration produced in the normal rotatory power of pure camphor by these solvents was proportional to the amount of the solvents present, so that $A$ represents the true rotatory power of camphor. With the last two solvents, however, it was found possible to express the rotation only by the more complicated formula $[\alpha] = A - Bq + Cq^2$.

The following are the solvents used and the formulæ arrived at:—

| | |
|---|---|
| Acetic acid ..... | $[\alpha] = 55{\cdot}49 - 0{\cdot}13729\ q$; |
| Ethyl acetate ..... | $[\alpha] = 55{\cdot}15 - 0{\cdot}04383\ q$; |
| Ethyl monochloracetate | $[\alpha] = 55{\cdot}70 - 0{\cdot}06685\ q$; |
| Benzene ..... | $[\alpha] = 55{\cdot}21 - 0{\cdot}1630\ q$; |
| Dimethylaniline ..... | $[\alpha] = 55{\cdot}78 - 0{\cdot}1491\ q$; |
| Wood-spirit..... | $[\alpha] = 56{\cdot}15 - 0{\cdot}1749\ q + 0{\cdot}0006617\ q^2$; |
| Alcohol ..... | $[\alpha] = 54{\cdot}38 - 0{\cdot}1614\ q + 0{\cdot}000369\ q^2$. |

Calculating from these formulæ the value of $[\alpha]$ for the limits $q = 0$ and $q = 100$, as in the previous paper, the following numbers are arrived at:

| Solvent. | $[\alpha]$ for $q = 0$. Pure camphor. | $[\alpha]$ for $q = 100$. Infinite dilution. | Total alteration. |
|---|---|---|---|
| Acetic acid..... | 55·5 | 41·8 | 13·7 |
| Ethyl acetate..... | 55·2 | 50·8 | 4·4 |
| Ethyl monochloracetate .. | 55·7 | 49·0 | 6·7 |
| Benzene ..... | 55·2 | 38·9 | 16·3 |
| Dimethylaniline..... | 55·8 | 40·9 | 14·9 |
| Wood-spirit ..... | 56·2 | 45·3 | 10·9 |
| Alcohol ..... | 55·4 | 41·9 | 12·5 |

The mean of the values thus obtained for the pure substance gives for the specific rotatory of camphor at 20°—

$$[\alpha]_D = 55{\cdot}6^\circ \mp 0{\cdot}4^\circ.$$

J. R.

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**Calorific Spectra.** By M. AYMONNET (Compt. rend., lxxxii, 1153—1156).

IN the spectrum yielded by an apparatus of flint glass, the position of the place of maximum temperature approaches the less refrangible end in proportion as the temperature of the source of heat is lowered. Flint glass becomes less diathermanous, and a solution of iodine in chloroform more so, when the temperature of the source is lowered.

R. R.

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**Theory of Crystals.** By E. MALLARD (Compt. rend., lxxxii, 1164—1167).

THE author proposes to account for certain optical anomalies in crystals, and for certain facts of dimorphism, by regarding the crystals as edifices formed on one and the same *framework* taken in different positions, and combined according to certain laws. The conclusion of his observations is that a single substance can have but one crystalline *framework*,—but one primitive form.

R. R.

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**Ratio of the Specific Heats in a Gas having Monatomic Molecules.** By YVON VILLARCEAU (Compt. rend., lxxxii, 1127—1130).

THE ratio of the two specific heats in a gas, the molecules of which are material points, incapable of internal actions and affected only by motions of translation, would, according to the thermodynamical theory of gases, be 1·66..... Experimental determinations of the value and of the ratio for certain gases have given the number 1·42...., and the difference has been attributed by the author to the complex structure of the molecules of these gases. He now draws attention to some researches of Kundt and Warburg, who, by measuring the distances of the nodes in pipes made to sound with air and the vapour of mercury respectively, were able to deduce the ratio of the two specific heats for the vapour of mercury, the value of the ratio for air being taken as 1·405. The number they thus obtained was 1·67, and the author considers this result as a confirmation, both of the dynamical theory of gases, and of the view generally taken by chemists as to the constitution of the molecule of mercury vapour.

R. R.

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**Thermochemical Investigations.** By JULIUS THOMSEN (J. pr. Chem. [2], xiii, 348—369).

*Gold and its Compounds.*—Gold shows allotropic peculiarities according to the kind of solution from which it is precipitated and the kind of reagent used. Three such modifications have been investigated. When gold is precipitated from a solution of the chloride by means of sulphurous acid, it forms a mass which balls together; when precipi-

tated in a similar way from a solution of the bromide, it forms a very fine dark powder, which retains its pulverulent state even on drying: when reduced from the sub-chloride, sub-bromide, or sub-iodide by sulphurous acid or a hydrogen acid, it has the form of a very fine powder with perfect metallic lustre and a yellow colour. These modifications differ from each other by unequal evolution of heat in similar reactions. The gold which has been precipitated from the chloride by sulphurous acid shows least energy and is taken as the standard of reference. The energy of gold precipitated from the bromide is greater by an amount represented by 3,200 heat-units, while that of gold precipitated from the sub-chloride, the sub-bromide, or sub-iodide is 4,700 units greater for each atom. The last two modifications, therefore, evolve respectively 3,200 and 4,700 units of heat when converted into the first modification.

The following tables give the results of the experiments on the thermo-chemistry of the compounds of gold:—

| Reaction. | Evolution of heat. | Explanation. |
|---|---|---|
| $(AuCl_3Aq,HClAq)$ ..... | 4530 units. | Reactions of halogen-acids on the soluble haloïd compounds of gold. |
| $(AuBr_3Aq,HBrAq)$ .... | 7700 ,, | |
| $(AuCl_3Aq,3HBrAq)$ .... | 15210 ,, | |
| $(AuBr_3Aq,3HClAq)$ .... | 4280 ,, | |
| $(AuCl_4HAq,4HBrAq)$ .. | 13800 ,, | |
| $(AuBr_4HAq,HClAq)$ .... | − 510 ,, | |
| $(AuO_3H_3,4HBrAq)$ .... | 36780 ,, | Heat of neutralisation of hydrated oxide for hydrobromic and hydrochloric acids. |
| $(AuO_3H_3,4HClAq)$ ..... | 22970 ,, | |
| $(AuCl_3Aq,2SO_2Aq)$ .... | 83600 ,, | Reduction of soluble haloïd compounds by sulphurous acid. |
| $(AuBr_4HAq,2SO_2Aq)$ .. | 61790 ,, | |
| $(3AuCl,HClAq)$ ..... | 4980 ,, | Decomposition of subchloride and sub-bromide by the corresponding halogen-acid. |
| $(3AuBr,HBrAq)$ ..... | 3650 ,, | |
| $(2AuBr,SO_2Aq)$ ..... | 42760 ,, | Reduction of sub-bromide and sub-iodide by sulphurous acid. |
| $(2AuI,SO_2Aq)$ ..... | 23400 ,, | |
| $(AuCl_3Aq,3KIAq)$ ..... | 45660 ,, | Neutral chloride decomposed by KI. |
| $(AuBr_4H,5H_2O,Aq)$ .... | −11400 ,, | Direct determination of heat of solution. |
| $(AuCl_3Aq)$ ..... | + 4450 ,, | |
| $(AuBr_3,Aq)$ ..... | − 3710 ,, | |
| $(AuBr_3{,}8HBrAq)$ ..... | + 3880 ,, | Indirect determination of same for $AuBr_3$. |

*Heat of Formation of Gold Compounds.*

| Reaction. | Evolution of heat. | Explanation. |
|---|---|---|
| $(Au,Cl_3)$ | 22820 heat-units. | Heat of formation of anhydrous haloïd compounds. |
| $(Au,Br_3)$ | 8850 ,, | |
| $(Au,Cl)$ | 5810 ,, | |
| $(Au,Br)$ | − 80 ,, | |
| $(Au,I)$ | − 5520 ,, | |
| $(Au_2,O_3,H_2O)$ | −13190 ,, | Heat of formation of hydrated oxide. |
| $(AuCl_3,Aq)$ | + 4450 ,, | Heat of solution. |
| $(AuBr_3,Aq)$ | − 3760 ,, | |
| $(AuBr_4H,5H_2O,Aq)$ | −11400 ,, | |
| $(AuO_3H_3,3HBrAq)$ | 29180 ,, | Heat of neutralisation of hydrated oxide for 3 and 4 molecules of halogen-acids. |
| $(AuO_3H_3,3HClAq)$ | 18440 ,, | |
| $(AuO_3H_3,4HBrAq)$ | 36780 ,, | |
| $(AuO_3H_3,4HClAq)$ | 22970 ,, | |
| $(Au,Cl_3,Aq)$ | 27270 ,, | Heat of formation of solutions of neutral haloïd compounds. |
| $(Au,Br_3,Aq)$ | 5090 ,, | |
| $Au,Cl_3,HClAq)$ | 31800 ,, | Heat of formation of solutions of acid haloïd compounds. |
| $(Au,Br_3,HBrAq)$ | 12790 ,, | |

G. T. A.

**Influence of Pressure on Combustion.** By V. WARTHA (J. pr. Chem. [2], xiv, 84—93).

THIS paper gives the results of the author's experiments on the burning of candles in air at various pressures. In one experiment several stearine candles were burned for a given time, first in air under the pressure of 1·95 atmospheres and then in air at the ordinary pressure. It was found that the loss of weight of the candles at the higher pressure was from 13 to 17·4 per cent. less than at the lower pressure. At the higher pressure the candles burned with a dull yellowish-red smoky flame, fully twice as long as that of the same candles burning in the open air.

Candles burned under the receiver of an air-pump in which the pressure of the air was kept at 90 mm. gave a large clear non-luminous flame, consisting of an inner bluish-green cone surrounded by a violet stratum, which in turn was enclosed in an almost invisible faint-violet envelope.

The author thinks that the differences observed in the burning of candles and other combustibles under varying pressures are due to the effect of pressure on the temperature of dissociation of the substances burned. Dissociation takes place at a lower temperature under a high then under a low pressure. Hence, in candles burning in air under greatly increased pressure, dissociation of hydrocarbons takes place more

rapidly than the products can be burned, notwithstanding the increased supply of oxygen, and a smoky flame results, whilst under reduced pressures the contrary holds good. Frankland's hypothesis, that in rarefied air the mobility of the molecules of oxygen is greater, so that they penetrate more freely into the interior of the flame and thereby reduce its luminosity, is regarded as improbable.

J. R.

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## Contributions to the Theory of Luminous Flames.

By K. HEUMANN (Liebig's Annalen, clxxxi, 129—153).

THE paper begins with an historical sketch of the theories brought forward to account for the facts concerning luminous flames. To Wibel's experiments, from which he concluded that increase of luminosity is brought about by increasing the temperature of the flame, objection is taken; but by new experiments arranged so as to remove all other disturbing influences, the author shows that increase of temperature is *one* of the causes of increase of luminosity of hydrocarbon flames, and *vice versâ*. At the same time experiments are described which show that dilution with indifferent gases also causes a diminution in the luminosity of hydrocarbon flames. These two causes are generally together at work in diminishing the luminosity of ordinary flames; yet it is possible, as shown by experiment, to increase luminosity by heating *only*, and to diminish luminosity by cooling *only*.

In the case of a gas flame burning in an atmosphere of oxygen, the decrease of luminosity is to be traced chiefly to rapid oxidation of the carbon to non-luminous gases (CO and $CO_2$). That this is so may be shown by causing a gas, the materials of which do not undergo conversion into gases which are non-luminous at the temperature of the flame, to burn in oxygen, when an extremely luminous flame results. Further by diluting the oxygen with an indifferent gas, as $CO_2$, a flame is produced more luminous than that obtained when pure oxygen is used. This dilution may be brought about by the products of combustion themselves, in which case the increase in luminosity is to be traced not only to decreased oxidation but also to lowering of temperature.

The author concludes that, in the case of hydrocarbon flames, decrease of luminosity is brought about by three causes, viz., decrease of temperature, dilution either of the burning gas or of the supporter of combustion, and increased destruction (by oxidation) of luminous matter, and that these three causes generally act simultaneously.

M. M. P. M.

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# Inorganic Chemistry.

**Production of Ozone by the discharge from the Electric Machine.** By C. GIANNETTI and A. VOLTA (Gazzetta chimica italiana, v, 439—451).

AFTER claiming the priority over Wright (*Science* [3], iv, 26) in using the Holtz machine for the purpose of producing ozone, and describing the apparatus he employed for that purpose, the authors proceed to describe the results they obtained on repeating his experiments. Wright had made no quantitative determination of the amount of ozone formed, but the authors found that it was but small, varying from ·80 to 1·99 milligrams per litre, when about three litres per hour were passed through the apparatus, according as the plate or the ball between which the brush discharge passed, was positive. On employing a ball and a wire brush in their ozone tube previously described (*Gazz. chim. ital.*, iv, 481), they obtained 1·7 and 4·5 milligrams of ozone per litre, according as the brush formed the positive or the negative pole respectively. As, however, the passage of sparks, which it is difficult to obviate, entirely decomposes the ozone, it is far better to employ an apparatus in which the action takes place by induction instead of the direct discharge. The authors have therefore adopted an apparatus somewhat similar to Thenard's, consisting of two glass tubes 1·8 and 2·5 centimeters wide and 25 centimeters long, placed one within the other, the smaller tube being coated on its inner surface with tin foil, and the larger on its outer surface; the gas to be operated on is passed through the annular space between the two tubes. This annular space is closed at each extremity by means of sealing-wax except where two small tubes pass through for the admission and exit of the gas; this was passed through the apparatus at a rate varying from about ·5 to 2·5 litres per hour in the various experiments, the armatures being connected with a Holtz machine, whilst sparks were taken between the conductors. Most of the experiments were made with oxygen, when it was found that, other things being the same, the production of ozone augmented with the electrical tension. A diminution of the velocity of the passage of the gas increased the production of ozone, a result which accords with that observed by Houzeau; a decrease in the temperature augments the production of ozone. In some of the most favourable results, when the oxygen was passing through the apparatus at the rate of from ·87 to ·44 litres per hour, it was found to contain from 36·5 to 38·25 milligrams per litre. The results obtained on substituting a Ruhmkorff's coil for the Holtz machine were far less satisfactory.

It was found, on submitting air to the action of induction, that no nitrous compounds were produced similar to those observed by Houzeau, so that the apparatus may readily be employed for producing ozone from atmospheric air.

C. E. G.

**On the Saturation of Air with Water-vapour, and on the Drying of Air.** By H. C. DIBBITS (Zeitschr. Anal. Chem., 1876, 121—170).

IN the first part of this paper experiments are described which prove that coal-gas becomes completely saturated with water-vapour by passing through a "wet meter." In the second part numerous experiments are detailed the general results of which are:—

(1.) Air which has been dried by means of concentrated sulphuric acid becomes completely saturated with water-vapour by passing through water at a maximum rate of 30 litres per hour.

(2.) Air dried as described may be saturated with water-vapour by being caused to pass over the surface of water, provided that the surface of water exposed be not very small compared with the rapidity of the flow of air.

The third part of the paper deals with the question of drying air; it is shown experimentally that when calcium chloride is the desiccating agent employed, temperature exerts a marked influence: that if air dried by passage over this salt at a given temperature be brought into contact with a fresh quantity of the same salt at a lower temperature, a further absorption of water takes place, but that if the second portion of calcium chloride be maintained at a higher temperature than the first, the air becomes moister. By passing a gas, already dried over calcium chloride, through a system of tubes containing equal weights of calcium chloride, positive or negative alterations in weight may be obtained, according as the different parts of the system possess a higher or lower temperature. If the temperature at the beginning of the system of tubes be the same as that at the end, the algebraic sum of the weight-alterations always = 0; if these two temperatures differ, the system suffers a positive or negative weight-alteration, in proportion to the difference of temperature between the first and last tubes.

The results of the author's experiments upon drying air by means of sulphuric acid and phosphoric anhydride are summarised as follows:—

1. If the absorption-tubes cannot be closed by means of ground-glass stoppers, it is better to weigh the tubes open than to close them by means of caoutchouc stoppers. If the connecting tubes be not very wide nor short, the error arising from the diffusion inwards of moist air is almost inappreciable. Larger errors are more liable to arise from an inequality, as regards temperature and humidity, between the outer glass surfaces and the air.

2. It is better, in exact estimations of water, to press than to suck the air through the tubes.

3. Concentrated sulphuric acid (containing not more than 8·4 per cent. water), dries air at temperatures up to about 25° so thoroughly that 100 litres do not give up to phosphoric anhydride more than 0·0002 gram.

4. If the temperature be higher than 25° or 30°, sulphuric acid does not so completely desiccate air: yet the quantity of water-vapour

contained in 1 litre of air dried by means of sulphuric acid at 50° amounted to less than 0·0001 gram.

Phosphoric anhydride may be said to effect an absolute desiccation of air.

The following table of the weights of water-vapour contained in 1 litre of saturated air is given by the author as being more exact than any generally found in the text-books.

The figures are calculated from the vapour tension determinations of Regnault and of Magnus.

| Temperature. | Weight of water-vapour in milligrams. Magnus. | Regnault. | Temperature. | Weight of water-vapour in milligrams. Magnus. | Regnault. |
|---|---|---|---|---|---|
| − 20° .. | 1·046 | 1·058 | + 1° .. | 5·131 | 5·209 |
| 19 .. | 1·136 | 1·146 | 2 .. | 5·495 | 5·570 |
| 18 .. | 1·234 | 1·241 | 3 .. | 5·881 | 5·953 |
| 17 .. | 1·338 | 1·342 | 4 .. | 6·291 | 6·359 |
| 16 .. | 1·450 | 1·450 | 5 .. | 6·725 | 6·789 |
| 15 .. | 1·571 | 1·567 | 6 .. | 7·185 | 7·246 |
| 14 .. | 1·701 | 1·693 | 7 .. | 7·672 | 7·730 |
| 13 .. | 1·839 | 1·829 | 8 .. | 8·188 | 8·242 |
| 12 .. | 1·988 | 1·975 | 9 .. | 8·733 | 8·784 |
| 11 .. | 2·147 | 2·131 | 10 .. | 9·310 | 9·356 |
| 10 .. | 2·317 | 2·299 | 11 .. | 9·919 | 9·961 |
| 9 .. | 2·499 | 2·481 | 12 .. | 10·563 | 10·600 |
| 8 .. | 2·694 | 2·676 | 13 .. | 11·243 | 11·275 |
| 7 .. | 2·901 | 2·886 | 14 .. | 11·960 | 11·987 |
| 6 .. | 3·122 | 3·112 | 15 .. | 12·716 | 12·738 |
| 5 .. | 3·358 | 3·355 | 16 .. | 13·514 | 13·531 |
| 4 .. | 3·610 | 3·617 | 17 .. | 14·355 | 14·366 |
| 3 .. | 3·878 | 3·898 | 18 .. | 15·240 | 15·246 |
| 2 .. | 4·163 | 4·201 | 19 .. | 16·171 | 16·172 |
| 1 .. | 4·466 | 4·527 | 20 .. | 17·152 | 17·147 |
| 0 .. | 4·788 | 4·868 | | | |

M. M. P. M.

## Selenium in Silver. By H. Debray (Compt. rend., lxxxii, 1156—1158).

Selenium, derived from the sulphuric acid employed in refining processes, is not unfrequently present in ingots of silver, the working properties of which it greatly impairs. Selenium may be detected in silver by dissolving, with the aid of heat, 100 grams of the metal in nitric acid of 34° B. The silver is then precipitated by hydrochloric acid, and the filtrate evaporated to dryness at a gentle heat. The selenium is contained in the residue, in the state of selenic acid, and when this has been boiled with a little hydrochloric acid, and a solution of sulphurous acid added to the liquid, a precipitate of selenium is thrown down.

R. R.

## Processes for Purifying Potassium Iodide from Iodate.

By G. PELLAGRI (Gazzetta chimica italiana, v, 423—425).

AFTER noticing the inconveniences that may arise from the employment of an iodide containing iodate as a medicine, and in some chemical reactions as ozone paper, the author states that a perfectly pure iodide may be prepared by decomposed barium sulphide with iodine and then exactly precipitating with potassium sulphate; this, however, is difficult. The iodate, in a dilute solution, may be completely reduced to iodide by boiling it with iron turnings, but this method does not answer well with concentrated solutions. The iodate in these, however, is easily reduced to iodide by the employment of a couple consisting of a plate of iron and one of copper united by a wire: a deposit of ferric oxide is formed which increases for about two days, when the green ferroso-ferric oxide begins to make its appearance; this is a sign that the reduction is completed. The author also proposes the use of sulphuretted hydrogen as a reducing agent, removing the excess with a drop or two of iodine solution, and neutralising with potash.

C. E. G.

## Preparation of Potassium Bicarbonate. By L. PESCI (Gazzetta Chimica italiana, v, 425—427).

THE author finds that the best method of preparing pure potassium bicarbonate free from chloride and nitrate, is to pass a current of carbonic anhydride to saturation through a solution of potassium hydrate in alcohol of 80 per cent. At first neutral carbonate is formed which withdraws the water from the alcohol, forming a dense stratum at the bottom of the vessel, but on continuing the passage of the gas this becomes pasty from deposition of crystals of the bicarbonate. The alcohol containing chlorides and nitrates is now decanted and replaced by a fresh quantity, the passage of the gas being continued, with occasional agitation, until the pasty precipitate becomes pulverulent and the liquid is saturated with carbonic anhydride. The bicarbonate, after being thoroughly washed with alcohol, is found to be quite pure.

C. E. G.

## The Quantivalence of the Metals of the Rarer Earths. By L. F. NILSON (Deut. Chem. Ges. Ber., ix, 1056—1061).

IN this paper the author attempts to deduce the quantivalence of metals from the composition of their chloroplatinates. He shows that chloroplatinates may be divided into the following groups:—

1. Those in which the chlorine of the platinum chloride is twice as much as that of the basic chloride. To this group belong the univalent and bivalent metals.

2. Those in which the chlorine of the platinum chloride is four-thirds of that of the basic chloride. This group includes the elements of which the double atom is sexvalent.

3. Those in which the chlorine of the platinum chloride equals

that of the basic chloride. To this group belong probably the quadrivalent elements.

Classifying according to these groups the known chloroplatinates of the rarer metals, the author finds that beryllium is bivalent, thorinum quadrivalent, and cerium, lanthanum, didymium, erbium, and yttrium sexvalent (double atoms); a result agreeing with that which he previously deduced from a comparison of the composition and properties of the selenites of these metals.

Three new chloroplatinates are described in the paper:—

*Ferric chloroplatinate*, $Fe_2Cl_6.2PtCl_4 + 21H_2O$, forms large yellow oblique four-sided prisms, which lose 10 mol. of water at 100°.

*Chromium chloroplatinate*, $C_2Cl_6.2PtCl_4 + 21H_2O$, crystallises in fine green four-sided deliquescent prisms, which give off 10 mol. of water at 100°.

*Indium chloroplatinate*, $In_2Cl_6.5PtCl_4 + 36H_2O(?)$, forms yellow oblique four-sided prisms, with oblique end-faces, deliquescing rapidly in the air and losing half their water at 100°.

J. R.

## Further Contributions to our knowledge of Beryllium (Glucinum). By A. Atterberg (Deut. Chem. Ges. Ber., ix, 856).

Supplementary to a former paper (*Berichte*, vii, 472). New compounds are the ether of beryllium chloride $BeCl_2 + 2(C_2H_5)_2O$ (large prisms); bibasic beryllium chloride, $BeCl_2 + BeO_2H_2$ (in place of the earlier $\frac{5}{3}$ basic); diberyllium phosphate and arsenate, $BeH.O_3.PO + 3Aq$, and $BeH.O_3.AsO + 2Aq$, and triberyllium arsenate, $Be_3O_3 2AsO + 6Aq$.

It is also shown that the platinocyanogen compounds of beryllium and magnesium do not crystallise together, nor the sulphate of beryllium with those of nickel and cobalt.

G. T. A.

## Ultramarine-crystals. By C. Grünzweig and R. Hoffmann (Deut. Chem. Ges. Ber., ix, 864—868).

A paper on ultramarine-crystals having been communicated by R. Hoffmann to the jury of the Vienna International Exhibition of 1873, was noticed by Wagner in the *Jahresbericht* for 1875, together with a later communication by E. Büchner (*Deut. Chem. Ges. Ber.*, vii, 989). Büchner stated, that on examining a sample of ultramarine under the microscope, he observed minute crystals of quartz, and he concluded from this that what Hoffmann and Grünzweig had supposed to be ultramarine-crystals, were, in reality, merely crystals of quartz which had become coloured by the ultramarine.

As these papers were given in the *Jahresbericht* only as short abstracts, Grünzweig and Hoffmann now republish their original paper, verbatim, believing this quite sufficient to disprove any doubts of their having mistaken quartz-crystals for ultramarine; but, as the recognition of small crystals by the microscope is always a difficult matter, they have embraced every opportunity which has been afforded them to obtain the opinions of other observers, and now supplement

their former paper by some remarks of Vogelsang and Knapp, the latter being *à priori* opposed to their views.

H. H. B. S.

## On Ultramarine.

By J. PHILIPP (Deut. Chem. Ges. Ber., ix, 1109—1115).

WHEN green ultramarine is heated to 160° with water in sealed tubes it assumes a fine bright-blue colour. Its weight, however, remains nearly the same (the water taking up only a small quantity of sodium-compounds), and its composition is unaltered. The author found, moreover, that sulphur exists in the same condition in blue ultramarine prepared in the wet way as in the green ultramarine from which it was obtained. The formation of blue ultramarine is, therefore, in no way dependent upon the oxidation of sulphur, as has been thought. The author concludes that the difference between the two ultramarines is due to the presence in the green substance of a small quantity of sodium sulphide, either mechanically mixed or chemically combined with it, on the removal of which the blue colour appears. He found that green ultramarine is actually formed by fusing blue ultramarine with sodium sulphate and charcoal.

J. R.

## On Amalgams.

By E. DE SOUZA (Deut. Chem. Ges. Ber., ix, 1050).

SODIUM amalgam containing excess of mercury, when heated to 160°, leaves the compound $Na_3Hg$: potassium amalgam under the same circumstances leaves $K_2Hg$. Both are silvery crystalline substances. The latter takes fire easily, resembling in this respect potassium hydride.

Lead, tin, zinc, cadmium, and bismuth retain mercury at 360°, but not at 440°. By heating amalgams in vapour of sulphur (*a*), mercury (*b*), and diphenylamine (*c*), the following compounds were obtained:—

| | | | | | |
|---|---|---|---|---|---|
| (*a*.) | $Au_9Hg$ | $Ag_{13}Hg$ | $Cu_{16}Hg$ | $K_2Hg$ | $Na_3Hg$ |
| (*b*.) | $Au_9Hg$ | $Ag_{11}Hg$ | $Cu_{14}Hg$ | $Pb_8Hg$ | |
| (*c*.) | $Au_8Hg$ | $Ag_4Hg$ | $Cu_{14}Hg$ | | |

J. R.

## Some Compounds of Niobium. By B. SANTESSON (Deut. Chem. Ges. Ber., ix, 854).

THE chief object of this paper is to describe some niobates and fluoniobates prepared by the author. Besides the two hydrates with 4 and 7 molecules of water to 3 of $Nb_2O_5$, the sodium salts of the former $Na_2O.Nb_2O_5 + 6Aq$ and $2Na_2O.3Nb_2O_5 + 9Aq$ have been analysed, while several salts of the latter with heavy metals have been prepared. Most of them, especially those of Zn, Mn, Cd, Co, Ni, accord with the general formula $M_5H_5F_{30}Nb_3 + 28Aq$. The ferro-salt and a second

nickel-salt correspond with the formula $M_3H_4F_{20}Nb_2 + 19Aq$. The copper salt is $Cu_2HF_{10}Nb + 9Aq$, and the mercury salt $Hg_3F_{20}Nb_2 + HgF_2 + 16Aq$. These salts are crystallisable from a solution of hydrofluoric acid, insoluble in water, and decomposed when heated with it.

G. T. A.

**Composition of Magnetic Pyrites.** By G. LINDSTROM (Deut. Chem. Ges. Ber., ix, 858).

THE composition of this body is best expressed by the formula $Fe_7S_8$: but, as Nordanskiöld suggests, it may consist of iron protosulphide with excess of sulphur as an unnecessary additional constituent. This would explain its varying composition.

G. T. A.

**Silicide of Platinum.** By A. GUYARD (HUGO TAMM) (Bull. Soc. Chim. [2], xxv, 510).

WINCKLER'S silicide of platinum, $PtSi_8$, appears to be simply a mixture of the two bodies; its formula is far removed from those of other compounds of platinum with the metalloïds.

When platinum dust is heated with crystallised silicon in fine powder in the proportion of 2 to 1, combination takes place at a red heat with some violence, some of the silicon gets thrown out of the crucible, and the remainder combines with the platinum, forming a compound which fuses at a somewhat higher temperature to a bright crystalline mass, metallic in appearance, and very brittle. The composition of this substance is $PtSi_2$, which approaches the composition of the boride of platinum analysed by Martins.

C. H. P.

## Mineralogical Chemistry.

**Crystallographic and Chemical Investigation of some Minerals containing Fluorine from Ivitule,' Greenland.** By A. E. NORDENSKIÖLD (Deut. Chem. Ges. Ber., ix, 858—862).

AN analysis of *Ralstonite* leads to the formula $RAl(OF)_4 + 2H_2O$. The mineral, which crystallises in octohedrons, may therefore be considered a spinelle in which water is present. *Thomsenolite* is assigned to a new crystallographic system, the "clinoquadratic." This system bears the same relation to the quadratic as the clinorhombic does to the rhombic, in that the ortho- and clino-diagonals are equal.

The following new minerals are described in the periodical from which the above is taken (*Ofv. af Geol. För. Stockholm*): *Nohlite* from Nohl in Westgothland, and *Blomstrandite* (urano-titano-niobate).

A gadolinite, rich in beryllium, comes from a new locality (Flora

Tuna). The mines of Langban produce numerous minerals which may be classified as oxides, silicates, and arsenates.

Among the oxides manganosite, MnO, occurs. Several of the silicates may be looked upon as altered bi- and monosilicates of manganese, but also, on account of their various basic constituents and the properties derived from them, as independent species. To the bisilicates of this kind belong marmairolite, hydrated hydrorhodonite, $RO.SiO_2 + H_2O$, and an anhydrous bisilicate, which, like the previous one, contains lithium. To the same class of bisilicates probably belongs the new mineral Ganomalite (γάνωμα, glazing), a silicate of lead and manganese in which the lead replaces manganese (PbO about 35 per cent.). Another peculiar mineral is Barylite, a silicate of barium and aluminium free from manganese, but not belonging to the felspar group. It contains 46 per cent. of BaO.

The arsenates of this locality are not less variable in composition than the silicates, whether they contain chlorine after the type of mimetite with manganese and calcium, replacing lead as in the case of hedyphane, or are free from chlorine, like berzeliite. The mineral described under the name of *Karyinite* (Greek nut-brown), is closely allied to this group, since it contains only ·07 per cent. of chlorine. Lead, calcium, and manganese are present in this mineral in almost equal quantities. To this class belong the basic salts, such as *chondroarsenite.* A very peculiar mineral is an unusually strongly basic chlorarsenate of lead, which has as yet been found in quantities too small to settle its exact composition.

At Nordmali, another of the Wermland mines, a very beautiful bismuth sulphide was found, which contains lead and iron, $FeS.2PbS.Bi_2S_3$. As yet it has received no name.

A mineral from Falun containing selenium, probably a mixture of metallic bismuth with $PbS,Bi_2S_3$, has been analysed by Atterberg, also two pseudomorphs—amorphous damourite after pyrophysalite, and pseudo-emerald after emerald.

*Vivianite earth* (used as a pigment) has been found at Wemdalen in Norrland.

Under the name of *Matricite*, a hydrated monosilicate is described, $2MgO.SiO_2 + 2Aq$, which is the matrix of spodiosite.

An analysis of *chondrodite* confirms the formula $5MgO.2SiO_2$ with fluorine in variable quantity in place of oxygen.

Nordenskiöld gives, as the probable formula of a copper ore from Ural, $5[2RO.(SiO_2,CO_2)] + 2(Fe_2O_3.3H_3O) + aq$.

The rocks at Taberg in the neighbourhood of Jönköping—the first source of vanadium—are shown to consist chiefly of olivine (in addition to magnetite) with particles of plagioclase disseminated through the mass. Amphibole and pyroxene are entirely absent.

Steenstrup has published a treatise to prove the terrestrial nature of the well-known Greenland iron, while Nordenskiöld maintains its cosmic origin.

G. T. A

## On a Calcareous Alabaster from Mexico. By A. DAMOUR (Compt rend., lxxx, 1085—1086).

THIS substance is known as *onyx of Tecali*. It has the appearance of the onyx alabaster from Africa. It exhibits wavy layers, of various colours, and takes a fine polish. Its colour is milk-white, pale-yellow, or pale-green. Some specimens have brownish-red veins, due to the presence of ferric oxide. It has a splintery fracture, and is often streaked with fluor spar. Its specific gravity is 2·77. It was found to contain manganese by adding cerosoceric nitrate to a solution of the alabaster in strong nitric acid, when, after some hours, the liquid assumed a wine-red colour, owing to the oxidation of the manganese by the ceric oxide. It consists of 89 per cent. of calcium carbonate, together with the carbonates of magnesium, iron and manganese, besides a small quantity of water, which is evidently mechanically retained.

W. R.

## Occurrence of Native Mercury in the Département de l'Hérault. By N. THOMAS (Compt rend., lxxxii, 1111).

THE author has found the source of the native mercury which he has noticed for the last twenty-seven years, in the detritus from the hill called "Bois de Cazilhac," in the Canton of Ganges (Hérault). Mercury is also often present in the detritus from a mountain forming part of the chain of Seranes, in the Canton of Saint-Martin-de-Londres (Hérault).

W. R.

## Analysis of Magnetic Native Platinum from Nischne-Tagilsk (Ural). By TERREIL (Bull. Soc. Chim. [2], xxv, 482).

THE native platinum treated with aqua-regia left an insoluble residue consisting of osmium-iridium, chrome iron, and a silicate. The silicate was evaporated by fusion with potash; the residue unaffected was then fused with caustic potash and nitre, which separated the iron and chromium. Nickel has not generally been found with platinum minerals; its presence in this sample is an interesting fact.

The following are the results of the analysis:—

| Platinum with traces of iridium. | Osmium-iridium and metals insoluble in aqua regia. | Silver. | Copper. |
|---|---|---|---|
| 81·02 | 3·33 | trace | 3·14 |
| **Iron.** | **Nickel.** | **Chrome iron.** | **Silica.** |
| 8·18 | 0·75 | 3·13 | 0·13 |

The chrome iron contained $Cr_2O_3$ 1·75, FeO 1·01, $Al_2O_3$ 0·37.

C. H. P.

**A New Mineral from the Pyrenees.** By E. BERTRAND (Compt. rend., lxxxii, 1167).

THIS is a hydrated silicate of manganous oxide, to which the author has given the name of Friedelite. It crystallises in the rhombohedral system, and has a very distinct cleavage perpendicular to the principal axis. It is translucent, and in thin layers transparent; exhibits powerful double refraction with a negative axis; colour, rose-carmine. Hardness, 4·75; density, 3·07. Analyses gave silica 36·12, manganous oxide with a little iron 53·05, magnesia and lime 2·96, water 7·87. Friedelite may be referred to the formula $4MnO,3SiO^2,H_2O$.

R. R.

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**Analysis of Manganese Peroxide.** By T. L. PHIPSON (Bull. Soc. Chim. [2], xxv, 9).

A SAMPLE of manganese-ore which is used in the laboratory and in metallurgical processes was found to contain—

| $H_2O$. | $MnO_2$. | $Mn_2O_3$. | $Fe_2O_3$. | $Al_2O_3$. | YO. | BaO. |
|---|---|---|---|---|---|---|
| 2·02 | 72·17 | 6·20 | 3·66 | 0·90 | 0·10 | 0·58 |

| CaO. | MgO. | PbO. | CuO. | $Bi_2O_3$. | NiO. | $Tl_2O$. |
|---|---|---|---|---|---|---|
| 4·07 | 0·24 | 0·14 | 0·09 | trace | 0·04 | 0·01 |

| $As_2O_5$. | $P_2O_5$. | $CO_2$. | $K_2O$. | $SiO_2$ and gangue. | F and loss. | |
|---|---|---|---|---|---|---|
| 0·15 | 0·35 | 3·20 | 0·70 | 4·00 | 1·44 | = 100 |

with traces of cobalt, zinc, indium, and lithium.

Some of the manganese probably exists as protoxide in combination with phosphoric or carbonic acid, and the yttria is probably present as phosphate.

C. S.

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**Olivine-rock, Serpentine and Eclogite of the Saxon Granulite District.** By E. DATHE (Jahrb. f. Min., 1876, 225—245).

SERPENTINE occurs in the Saxon granulite district as a secondary rock, and as transitions occur between it and the granulite, it was supposed by Herm. Müller (*Jahrb. f. Min.*, 1846, p. 269) to be derived from the latter; others said it was derived from gabbro, and the Greifendorf serpentine was said by Müller (*Jahrb. f. Min.*, 1846, p. 284) to be derived from eclogite. Zirkel, however, first contended that Greifendorf serpentine was derived from olivine (*Mikros. Beschreibung.*, 1873, p. 311), and Sandberger (*Jahrb. f. Min.*, 1866, p. 385; 1867, p. 171) and Tschermak (*Sitzungsbericht. d. k. Akad. d. Wissenschaft*, 56, 1867) were of the same opinion. According to the law of J. Roth (*Ueber. d. Serpentine*, Berlin, 1870), serpentine may be derived from other minerals than olivine, viz.: non-aluminiferous augites and hornblendes. The author therefore considered it interesting to ascertain, by a thorough examination of the eclogite and serpentine of the granulite district, whether the latter was derived from the former. In the course of these examinations it was ascertained that the greater part

of the rocks consisted of olivine, and from it the serpentine was mostly derived. The author gives the results of his investigations under three heads:—1. Olivine-rock; 2. Serpentine; 3. Eclogite.

I. *Olivine-rock.*—This rock exhibits marked differences of composition, it may therefore be sub-divided into two groups: garnet-olivine-rock and enstatite-olivine-rock or enstatite-rock.

1. *Garnet-olivine-rock from Heiersdorf.*—Occurs in masses as large as a man's fist, 60 meters above the right bank of the river Mulde. Outwardly it has the appearance of trap-granulite, but a closer examination shows it to consist of light-brown or light-green grains, having a vitreous lustre, and also small black crystals with brilliant faces. Thin sections of this rock were prepared, and examined microscopically, with the following result:—

The predominating constituent is olivine, occurring in irregular grains and seldom exhibiting definite crystal sections; it is unusually fresh; many of the grains or individuals are penetrated by irregularly diverging cracks. Again, on other individuals these cracks follow the direction of the most perfect cleavage ($\infty \breve{P} \infty$). No formation of serpentine was observed to any extent, but owing to the cracks the rock was already disposed to form it, when the olivine becomes dull and converted into a granular or fibrous serpentine mass. On examining the cracks under polarized light, slight traces of this first stage of decomposition are apparent. Very few enclosures were observed in any of the olivine specimens, the commonest being extremely small olivine individuals or minute hollow spaces arranged in rows: occasionally, however, small opaque crystals were observed which were picotite or chromite. Besides olivine, enstatite is undoubtedly present, recognisable by the rectangular cleavage of the individuals and their optical properties, which prove the crystals to be rhombic. Magnesia-mica is occasionally found in the rock and always in the neighbourhood of the garnet, associated with disintegrated substance. All the minute light-red garnets are metamorphosed by atmospheric action, only a very small minority being partially decomposed; the product of this partial decomposition consists of colourless needles of asbestus, having a position perpendicular to the garnet-kernel. The majority of the garnets are completely decomposed, consisting entirely of radiating fibrous material which sometimes assumes more definite forms, such as twisted spiral leaves, appearing pale-blue in polarized light and of a greenish hue in transmitted light, at the same time exhibiting a slight dichroism, and between these leaves a deposit of magnetic-iron is observed. The undecomposed garnet substance is penetrated by irregularly disposed cracks: extremely small garnets are enclosed in this substance, also sharply-defined olivine crystals exhibiting the combination $\infty P . \infty \breve{P} \infty$; they are, however, more altered in composition than the olivine grains. Zircon occurs as a light-brown, transparent, narrow border to the opaque grains, or else as a delicate streak in the middle of them. No crystalline zircons were discovered.

2. *Garnet-olivine-rock and Diallagite-olivine-rock of Mohsdorf.*—The beds of rock on the river Chemnitz, at Mohsdorf and Dietendorf, were formerly supposed to be trap-granulite, but are now known to contain

olivine. The chief part of these beds consist of a massive dark green rock, which does not contain many large crystal individuals. Garnets are disposed throughout in streaks, thus giving to the whole an appearance closely resembling trap-granulite, but in reality approaching the garnet-olivine-rock of Heiersdorf. The chief constituent is olivine in large rounded grains, almost free from cracks, and unusually fresh; small grains of olivine also occur in enormous quantities. The latter are more or less decomposed, full of cracks, which are surrounded and filled with a brownish or green granular mass of serpentine. Small octohedral crystals of picotite or chromite are observed enclosed in the olivine. The rock is further intersected by light green, long crystalised individuals of enstatite, which are penetrated by cracks parallel to $\infty \breve{P} \infty$, and often enclose minute olivine crystals. Diallagite also occurs; magnesia-mica and chloritic substance occur as leaves and fibres in rosette-like aggregations, being the products of the decomposition of the garnet substance. Diallagite occurs in the principal olivine rock of Mohsdorf in the place of garnet; the longitudinal slits are perfectly straight and united by oblique slits passing from one to the other. A slight decomposition has taken place on these slits, the product being a grey powder consisting of calcium carbonate. Garnet is almost entirely absent, and it is observed that the olivine is more decomposed by the atmosphere in consequence, serpentine filling the small slits in the olivine mass. An analysis of this rock shows it to have the following composition:—

| $SiO_2$. | MgO. | CaO. | FeO. | $Fe_2O_3$. | $Al_2O_3$. | MnO. | $H_2O$. | |
|---|---|---|---|---|---|---|---|---|
| 41·990 | 31·490 | 1·841 | 1·659 | 9·143 | 6·734 | traces | 7·094 | = 99·951 |

*Enstatite-olivine-rock of Russdorf.*—The mass of serpentine marked in Naumann's geognostic chart of Saxony (Table XV), is situated south-east of Russdorf. It contains much enstatite, the individuals often attaining a length of 1 cm., and being parallel with each other. The mass of the rock is very fine-grained, and of a light green colour. Olivine grains are also present, being in fact the chief constituent of this rock. These grains are quite fresh, and almost entirely free from the characteristic slits or cracks, and partial decomposition; only the surface of the rock itself shows a slight alteration, the product being a light yellow to brownish granular substance, which seldom develops into fibrous serpentine. Occasionally, however, some of the olivine grains are slightly altered on their margins, a light yellow homogeneous serpentine being formed. The smallest olivine grains are the most decomposed, and enclosures similar to those mentioned in the other olivine rocks are observed in the olivine individuals. Enstatite also occurs, exhibiting a fine striation parallel to $\infty \breve{P} \infty$; also the larger individuals enclose rows of small olivine grains parallel to the same face, along with small, narrow, black, hollow spaces, which have the appearance of needles; there are also colourless hollows of the same size, so that it is probable that the dark ones owe their colour to the deposition of pulverulent substance, either at one end of the hollow or at the side, and are not solid bodies.

II. *Serpentine.*—This mineral occurs widely distributed in the Saxon

granulite district, particularly at Waldheim, Greifendorf, Reichenbach, Langenberg, Tirschheim, and Callenberg. The position of the beds is always uniform with that of the accompanying rocks, following their "dip" and "strike," but the serpentine is in reality only a secondary member of the formation. Some of the beds are several hundred metres in thickness, whilst others are not more than ten metres thick. It alternates with normal granulite, and the so-called trap-granulite, also with eclogite, sometimes stretching far away in the rock; at other times it appears like a very small, flat, interposed lens. Each bed of serpentine is built up of innumerable layers or plates of varying thickness, and cracks penetrate the whole. Chlorite and talc occur in the cracks and on the planes of stratification, resulting in veins of chlorite penetrating the mass in every direction, and with them occur magnesia-mica, actinolite, waldheimite, asbestus, steatite, precious serpentine, picrolite, dermatine, limbachite, pycnotrope, calcite, pearlspar, heavy spar, chalcidony, opal, iron-flint, chromite, magnetite, and limonite. The author examined the specimens of serpentine microscopically from different districts in the granulite mountains, and arranged them all under two heads, viz., garnet-serpentine and bronzite-serpentine.

1. *Garnet-serpentine.*—This sub-group includes more than half of all the serpentine in the district.

*Serpentine of Waldheim.*—Contains, besides decomposed garnet (apparent to the naked eye), many light, lustrous spots, sometimes 6·5 mm. in length, and 4·5 mm. in breadth, which prove to be olivine. They are penetrated on all sides by rifts or cracks, which are spotted with a light yellow or greenish substance. The decomposed garnets are penetrated by greyish-white elongated leaves, radiating from the centre of each kernel, and having a pale blue colour in polarized light. A few crystal sections of a pale blue colour, with parallel longitudinal slits are also apparent, which no doubt are diallagite, as their optical "chief sections" are oblique to the plane of cleavage. Picotite or chromite is also present.

*Serpentine from the Quarry at the Gebersbach, Waldheim.*—Chiefly interesting because eclogite occurs with it in layers. Large olivine grains occur, accompanied by the most minute olivine fragments, the former being only slightly decomposed, but the latter are surrounded by broad streaks of serpentine. Next to them are spots where the yellow serpentine has assumed a reticulated structure; the single meshes (so to speak) are more sharply defined, on account of the deposition on them of a fine black powder, which sometimes has a dirty-red colour, and no doubt consists of ferric oxide. Diallagite is scarce in this specimen.

*Serpentine of the Breitenberg, Waldheim.*—Exhibits various degrees of colour and hardness, four distinct layers being observed, viz., two dark layers, alternating with two layers of a light green colour. The two dark layers are hard and brittle, contain garnet, and closely resemble the serpentine from Waldheim Tunnel and the Gebersbach, in every particular; whilst the green layers are characterised by their greater softness, and the entire absence of garnets, exhibiting at the same time a very decided reticulated structure, each mesh containing the remains of an olivine grain, surrounded by chrysotil and black

earthy particles. In every part of the section pseudomorphs of serpentine after olivine were observed. In the lower green layer larger grains of chromite, of the size of a pea, are disseminated; also crystals of bastite, enstatite, and specular iron, with a tolerably large deposit of powdery substance (limonite, &c.). From microscopical examination the author concludes that the serpentine of Breitenberg has two sources of derivation, viz., 1st, from garnet-olivine rock; and 2nd, from enstatite-olivine rock.

*Serpentine of Gilsberg.*—On the left side of the valley, near Gilsberg, a great mass of serpentine is observed, which here and there contains dark brown hornblende crystals, remarkably fresh olivine grains lying between the hornblende crystals, decomposed garnets containing magnesia-mica, diallagite, chromite, and iron-pyrites accompanying hornblende. This specimen also exhibited here and there a reticulated structure, and was essentially a garnet-serpentine.

*Serpentine of Crossen, near Mittweida.*—Closely resembles that from Gilsberg, the hornblende individuals being accompanied and often penetrated by magnesia-mica, which sometimes appears exfoliated. The author considers the magnesia-mica to be a secondary formation, as it occurs sometimes outside the cracks and next to chrysotil, and has therefore been formed in the same way as when it occurs in large cracks or clefts in the immediate neighbourhood of chlorite. Decomposed garnets and small olivine grains are present.

The author found that more than thirty other localities furnished serpentines having an almost identical constitution with those already described. A table is given, with remarks concerning the various colours, accessory minerals, and olivine remains occurring in the different serpentines, with the approximate amount of pulverulent magnetic oxide of iron which has separated out. There can be little doubt that all garnet-serpentine rocks have been formed from garnet olivine rocks by the action of water containing carbonic acid gas in solution upon them, the olivine being decomposed into a hydrated silicate of magnesium (serpentine) and ferrous oxide, which settles down between the serpentine substance, either as hydrated ferric oxide, or magnetic oxide. The amount of ferric oxide, &c., separated out is inversely proportionate to the amount of olivine residue still present in the rock, and directly proportionate to the amount of reticulated serpentine observed. The light green and leek-green varieties contain very little olivine, whilst the dark green serpentines are rich in olivine. As chrome-iron often occurs in large quantity in serpentine rock, the author considers that the brown, translucent, regular grains observed in some of the serpentine specimens, are chromite and not pictotite, finding them both translucent (a result not agreeing with the observations of H. Fischer, *Kritische Mikrosk. Min. Studien*, 1869, p. 21, who states that chromite is opaque). Picotite was formerly considered to be translucent, and was accordingly distinguished from chromite by that characteristic.

C. A. B.

### The Lavas of Thera. By M. Fouqué (Compt. rend., lxxxii, 1141—1143).

This paper summarises the results of a minute study of the geological relations and mineralogical character of these lavas. The distinction of the species of felspar, and the presence together of several triclinic felspars are noted; and there are also some new observations on the structure of lavas, and on the mode in which tridymite may be produced in volcanic rocks.

R. R.

### The Solid Carbon Compounds in Meteorites. By J. L. Smith (Chem. News, xxxiii, 196, 205, 217).

The author points out the general resemblance in the mineral constituents of the carbonaceous, or black meteorites, and those of the stony meteorites. He has examined a mass of carbonaceous matter, weighing 92 grams, taken from the interior of the Sevier meteorite. The specific gravity of this mass was 2·26; treated with ether it yielded a small quantity of crystals, which appeared to consist of either a sulphydrocarbon or free sulphur with a hydrocarbon. Bisulphide of carbon extracted a further quantity of the same crystals. Nitric acid removed *troïlite* from the mass, and the residue treated with nitric acid and potassium chlorate yielded graphitic oxide. The author concludes that this graphite occupies a position intermediate between graphites proper and ordinary carbon, but much nearer to the graphites. The carbonaceous meteorite of Orgueil yielded results very similar to those detailed; the carbon in such meteorites is regarded by the author as having a similar origin to that found in the irons. He cannot accept the hypothesis that the carbon is allied to humus; but rather inclines to the view that it approaches in nature the so-called hydrated carbon of Schutzenberger.

M. M. P. M.

## Organic Chemistry.

### Absorption of free Nitrogen by Organic Substances. By M. Berthelot (Compt. rend., lxxxii, 1283—1285).

Free nitrogen is absorbed by organic compounds at the ordinary temperature, under the influence of the silent electric discharge.

*Benzene* (1 gram) absorbs in a few hours 4—5 c.c. of nitrogen, forming a solid resinous compound, which evolves ammonia when strongly heated. But ammonia does not exist as such either in the compound or in the residual gas.

*Oil of turpentine* absorbs nitrogen slowly, likewise forming a solid, resinous compound, which evolves ammonia when heated.

*Marsh-gas* behaves similarly, yielding a solid nitrogenous product,

which evolves ammonia when heated. The uncondensed gas also contains ammonia.

With *acetylene* the principal product is a polymeric substance, previously discovered by Thenard. No hydrocyanic acid is formed.

The author points out that it is highly probable that reactions similar to the above go on in the air during storms, and whenever the atmosphere is charged with electricity, the organic matters then in contact with air absorbing nitrogen and oxygen, and becoming condensed. He suggests that this action of electricity may give rise to physiological changes playing a part in the peculiar disorders which affect human beings during storms.

J. R.

## A Convenient Method of obtaining Condensed Hydrocarbons. By WATSON SMITH (Deut. Chem. Ges. Ber., ix, 467).

THE author has previously shown that when vapour of naphthalene is passed through a tube heated to redness, hydrogen is eliminated and a condensed hydrocarbon (isodinaphthyl, $C_{10}H_7—C_{10}H_7$) is formed, which stands in the same relation to naphthalene as diphenyl to benzene.

The same substance is produced in much larger quantity when vapour of napthalene mixed with that of antimony trichloride is passed through a glass tube heated to bright redness. The reaction is represented as follows:—

$$6C_{10}H_8 + 2SbCl_3 = Sb_2 + 6HCl + 3\left|\begin{matrix}C_{10}H_7\\C_{10}H_7\end{matrix}\right..$$

Isodinaphthyl crystallises from benzene, &c., in thin colourless tables, melting at 186°—187°.

Tin tetrachloride acts still more easily than antimony trichloride, but in this case the isodinaphthyl formed appears to be accompanied by chlorinated products.

Other hydrocarbons are easily acted on by the same means; benzene, for instance, yielding with tin tetrachloride a large quantity of diphenyl.

J. R.

## Some New Octyl Derivatives. By W. MÖSLINGER (Deut. Chem. Ges. Ber, ix, 998—1008).

THE bodies described in this paper were obtained from the ethereal oil of *Heracleum sphondylium*. The oil consists for the most part of the acetic, caproic, and other ethers of primary normal octyl alcohol, and readily yields that alcohol by saponification.

*Octyl iodide*, $C_8H_{17}I$, is best obtained by passing dry hydrogen iodide into octyl alcohol to saturation and afterwards heating the liquid to 100° in closed vessels. The product contains 90 per cent. of pure octyl iodide boiling at 218°—222°.

*Octyl ether*, $(C_8H_{17})_2O$.—This body was obtained by mixing equivalent quantities of sodium octylate (formed by the action of sodium on

octyl alcohol) and octyl iodide, and heating the mixture to 100° for some time. It is a transparent oily-looking liquid, of specific gravity 0·805 at 17°, and boiling at 280°—282°.

*Octyl-ethyl ether*, $C_8H_{17}.C_2H_5.O$, formed by heating together equivalent quantities of sodium octylate and ethyl iodide, is a colourless mobile liquid of agreeable odour, boiling at 182°—184°. Specific gravity 0·794 at 17°; vapour density, 78·79.

*Octyl sulphide*, $(C_8H_{17})_2S$.—Octyl chloride and potassium sulphide in alcoholic solution rapidly decompose each other when heated together. The octyl sulphide thus formed is a slightly yellow mobile liquid having a peculiar alliaceous odour and boiling with decomposition above 310°. Specific gravity 0·8419 at 17°. It forms a crystalline compound with mercuric chloride.

*Barium octylsulphate*, $(C_8H_{17}SO_4)_2Ba$, formed by carefully mixing equal weights of pure strong sulphuric acid and octyl alcohol, and after 24 hours neutralising the mixture with barium carbonate, crystallises in thin pearly laminæ, which decompose at 100°, giving off octylene. The salt is very sparingly soluble in water.

*Potassium octylsulphate*, obtained by decomposing the barium salt with potassium sulphate, is a white indistinctly crystalline mass, soapy to the touch, and easily soluble in water.

*Octyl phosphine*, $C_8H_{17}.H_2.P$.—This body is formed when a mixture of phosphonium iodide, octyl iodide, and zinc oxide is heated to 160°—180° in sealed tubes. It is a transparent mobile liquid, highly refractive, and having the powerful stupefying odour of all phosphines. Its boiling-point is 184°—187°, specific gravity 0·829 at 17°. It absorbs oxygen from the air, but only slowly, the process going on for several days. The substance thereby formed is an acid intermediate between octylphosphine and the corresponding phosphinic acid, and hence may be termed *octylphosphinous acid*. Its silver salt is a white curdy precipitate, which is reduced by heat.

Octylphosphine in the pure state is very violently attacked by fuming nitric acid, but when diluted with glacial acetic acid the action proceeds quietly, the product being octylphosphinic acid, a body which dissolves in hot glacial acetic acid and separates as the solution cools in a spermaceti-like mass.

Octylphosphine is easily soluble in alcohol, benzene, and chloroform, but insoluble in water and in sulphuric, nitric, and hydrochloric acids, with which it does not combine. It forms a solid compound, however, with hydriodic acid.

J. R.

## On Allyl Borate.

By C. Councler (Deut. Chem. Ges. Ber., ix, 485—487).

This substance is formed in small quantity when boron trichloride is passed into absolute allyl alcohol, and more abundantly when a mixture of boric anhydride and allyl alcohol is heated to 130° in sealed tubes. The product is a colourless liquid resembling common alcohol and having a tear-exciting odour. It burns with a green flame and is instantly decomposed by water, boric acid being separated. It boils

between 168° and 175°. Its composition agrees with the formula, $B(OC_3H_5)_3$.

J. R.

**Action of Zinc-ethyl on Aldehyde.** By E. WAGNER (Bull. Soc. Chim. [2], xxv, 396).

BEILSTEIN and Rieth concluded from their experiments that acetal was obtained on decomposing with water the zinco-organic compound obtained by the above reaction. The author repeated the experiment in the following manner:—A flask connected with an inverted condenser contained the zinc-ethyl and a little aldehyde, and it was observed that the reaction took place, even in the cold, but was completed at a gentle heat. On cooling, the flask was filled with crystals of the zinco-organic compound, and on decomposing this with water, an oil was obtained which, on being heated with moist silver oxide and carefully dried, furnished a product distilling between 96° and 99°. This proved to be methylethyl carbinol. On combining this alcohol with hydriodic acid, a product was obtained having a boiling-point of 119°—120°, and on oxidising the latter with potassium bichromate and sulphuric acid, a ketone distilling at 180° was obtained together with acetic acid.

C. A. B.

**Retort for Preparing Ketones and Aldehydes by the Distillation of Calcium Salts.** By E. TER MEER (Deut. Chem. Ges. Ber., ix, 844).

IN the distillation of solid or semi-solid substances, as of a mixture of calcium butyrate and formate for butyl aldehyde, or calcium camphorate for camphor-phorone, it has been found that but small quantities can be distilled at once in an ordinary retort, as the outside portions are apt to become strongly overheated and burnt, whilst those farthest from the source of heat are, it may be, still insufficiently heated. In such cases a complete distillation (without loss) is next to impossible.

It was found, however, that if the substance to be subjected to distillation were spread upon a plate in a thin layer, and a kind of funnel-shaped head with condensation-tube inverted over it, the distillation proceeded to much greater advantage.

A retort combining all the advantages of such an arrangement has been constructed by E. ter Meer in Prof. V. Meyer's laboratory in Zürich. It is constructed of copper, is very shallow, flat-bottomed, circular, has a lid with slight rise from the circumference to the condensation-tube, and secured by screws in the usual way.* One kilo. of the mixed calcium butyrate and formate distilled in quantities of 50 grams at a time yielded 270 grams of dry crude aldehyde (butyric). In small quantities of 10 grams each, Lieben and Rossi obtained from an equal weight of the mixed salts, using small glass retorts, *about* 250 grams of the aldehyde, but 100 distillations were required

* *Note by Abstractor.*—This retort in principle appears to be precisely similar to those used in the distillation of pitch and in the rectification of phenol, and the object aimed at in both cases is nearly the same.

against only 20 with the copper retort. After each distillation the copper retort was found to contain a loose porous residue of pure white calcium carbonate, which was very easily removed.

W. S.

**Formation of Lactide-bromal.** By E. KLIMENKO (Deut. Chem. Ges. Ber., ix, 967).

BROMAL reacts with lactic acid, when heated with it over the water-bath, to form a crystalline substance, having the formula $C_5H_5Br_3O_3$, and identical in properties with the body previously obtained by the author by the action of bromine on an ethereal solution of lactic acid (see this Journal, 1876, i, 900).

J. R.

**Transformation of Olefines into the corresponding Alcohols.** By A. BOUTLEROFF (Bull. Soc. Chim. [2], xxv, 395).

THE analogy which exists between the terebenes and heptene obtained from pentamethylethol, led the author to endeavour to produce a combination of heptene with water, under similar conditions to those by which terpene hydrate is obtained from terebenthene. Crystals of pentamethylethol were obtained in the above manner. Isobutylene produced trimethyl carbinol on being heated with concentrated nitric acid and water containing one-tenth of its bulk of alcohol in a sealed tube. Dilute sulphuric acid may be substituted for the nitric acid, the same effect being produced. In the experiment, the liquid hydrocarbon is mixed with twice its volume of the diluted acid, and heated at 100°; a diminution in the volume is eventually observed, and di-isobutylene is formed. The author concludes that the other olefines can be converted into the corresponding alcohols by this process.

C. A. B.

**Preparation of Glycol.** By ERNST BÖRNSTEIN (Deut. Chem. Ges. Ber., ix, 480—482).

THE author has experimented on Demole's method of preparing glycol, which consists in boiling together ethene bromide, potassium acetate, and 90 p.c. alcohol. He thus obtained only monacetin. The Zeller-Huefner process, with potassium carbonate and water, yielded pure glycol.

J. R.

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**On a supposed case of Molecular Transformation in the Fatty Series.** By E. DEMOLE (Deut. Chem. Ges. Ber., ix, 743—747).

BAUMSTARK recently described as an ethidene-compound a body obtained by passing ethene into an alcoholic solution of iodine at 65° (see this Journal, 1875, 140). The author, doubting the correctness of Baumstark's conclusions as to the constitution of the body, has re-

peated the experiments and arrived at identically the same results with regard to its composition and properties. He has, however, succeeded in obtaining the same body synthetically by replacing the group (OH) in monethylglycol, $CH_2(OH) - CH_2OC_2H_5$, by iodine, which result was effected by acting on monethylglycol with phosphorous odide, $PI_3$. Baumstark's substance must, therefore, be regarded as a derivative of ethene, not of ethidene. Its constitutional formula is $CH_2I - CH_2OC_2H_5$. Whence it appears that ethene iodide reacts with alcohol at 65° to form hydriodic acid and the new body, *ethene iodethylin.*

J. R.

## Isobutene Chlorhydrate. By L. Henry (Bull. Soc. Chim., xxv, 23—24).

Isobutene combines readily with hypochlorous acid and forms a chlorhydrate boiling at 128°—130°, which, when oxidised with nitric acid, yields a chlorobutyric acid boiling at about 190°. From this it follows that the chlorhydrate has the constitution $(CH_3)_2CCl.CH_2OH$, and therefore, in this case, the addition of hypochlorous acid follows also the law which the author has previously established, *i.e.*, that the chlorine combines with the carbon-atom containing the least, and the hydroxyl with that containing the most hydrogen.

C. S.

## Influence of Acids and Salts on the Inversion of Cane-sugar. By M. C. Fleury (Dingl. polyt. J., ccxix, 436).

The equation of an inversion curve (so far as acid is concerned), may be expressed thus :—

$$1 - y = [k\ \mathrm{f}\ (a) - x],$$

where $k$ is a coefficient dependent on the nature of the acid and on the temperature, and f $(a)$ a function of the quantity of acid. It is supposed that the quantity of inverted sugar is proportional, at each moment, to the quantity of substance present in the liquid. The experiments confirm the view that the products of inversion—glucose and lævulose—exhibit no tendency to become re-associated, at least not in presence of the acid.

When potassium sulphate and aluminium sulphate act on sugar, these salts undergo decomposition, the latter salt progressively. Ammonium salts and the alkaloid salts generally bring about no inversion.

M. M. P. M.

## On a new Crystalline Organic Substance called Raffinose. By E. Loiseau (Compt. rend., lxxxii, 1058—1060).

This body was obtained from sugar from the refinery of Messrs. A. Sommier and Co., in course of an investigation on the extraction of sugar from molasses with sucrate of lime. It has hardly any sweet taste. It crystallises well in transparent crystals. When dry, it is

almost insoluble in 90 per cent. alcohol. At 20° water dissolves one-seventh of its weight of raffinose, and at 80° any quantity. It liquefies when heated to 80° in a sealed tube. It loses 15·1 per cent. of water at 100°, but reabsorbs it gradually when cold. Its rotatory power, compared with sugar equal to 100, is 159. Its formula is $C_6H_4O_7$, or a multiple thereof. If the water it loses be excluded from the formula, it is $C_9H_{16}O_8 + 2\frac{1}{2}H_2O$.

W. R.

## Action of Hydriodic Acid on Quercite. By L. Prunier (Compt. rend., lxxxii, 1113—1116).

On distilling 10 grams of quercite with 400 grams of hydriodic acid saturated at 0°, a liquid was obtained which was found to consist of a small portion which distilled between 60° and 70°; *benzene*, in considerable quantity, the presence of which was clearly proved by its boiling point, by its conversion into nitrobenzene, and subsequently into aniline; and several hydriodic ethers, probably also oxyphenol (? pyrocatechin) and hydroquinone. These last bodies differ from quercite, $C_6H_{12}O_5$, only by the elements of 3 molecules of water.

W. R.

## Action of Saliva on different kinds of Starch. By Lefberg and Georgieski (Bull. Soc. Chim. [2], xxv, 393).

The authors draw the following conclusions from their experiments:—

1. Potato-starch is converted more easily into sugar by the action of saliva, than wheaten starch.
2. Maize-starch occupies a place between potato-starch and wheaten-starch.
3. Soluble starch behaves in the same way as potato-starch.

C. A. B.

## Action of some Metallic Bases on Monochloracetic Acid. By G. Schreiber (J. pr. Chem. [2], xiii, 436—475).

Heintz has shown that monochloracetic acid, when heated with potash, yields glycollic acid, and that when boiled with excess of calcium hydrate, it yields the same product together with diglycollic acid. The author has examined the behaviour of some other bases. In his experiments the monocloracetic acid employed was mixed at once with *excess* of the base, and boiled for 12—36 hours in a retort connected with a reversed condenser.

*Lithium Hydrate.*—The product of the action of this base on monochloracetic acid is chiefly diglycollic acid, with a very small proportion of glycollic acid.

Lithium diglycollate forms small transparent crystals or delicate needles, which dissolve in 2·2 parts of water at 18·5°. The crystals have the formula $C_4H_4O_5Li_2 + 5H_2O$; but when their concentrated aqueous solution is covered with alcohol, crystals containing only $2\frac{1}{2}$ mol. of water are obtained.

*Magnesia* boiled with water and monochloracetic acid produces glycollic and diglycollic acids. Magnesium glycollate, $C_4H_6O_6Mg + 2H_2O$, dissolves in 12·6 parts of water at 18°, and much more freely in boiling water.

*Barium hydrate*, boiled with monochloracetic acid, produces only diglycollic acid. Barium diglycollate, $C_4H_4O_5Ba + H_2O$, crystallises in small needles, which require for solution about 600 parts of water at 100°. It appears to yield an acid salt by treatment with sulphuric acid.

*Strontium hydrate* produces diglycollic acid, together with a very small quantity of glycollic acid. Strontium diglycollate, $C_4H_4O_5Sr + 4H_2O$, forms small crystals, sparingly soluble in water. The crystals are resolved by boiling with water into a crystalline powder having the formula $C_4H_4O_5Sr + 2\frac{1}{2}H_2O$. Strontium glycollate, obtained by dissolving strontium carbonate in glycollic acid, crystallises in microscopic needles containing 5 mol. of water. It dissolves in 30 parts of water at 19°.

*Aluminium hydrate* and *stannous hydrate*, when boiled with monochloracetic acid, produce only glycollic acid.

*Zinc oxide* produces only glycollic acid. Zinc glycollate, $(C_2H_4O_2)_2Zn + 2H_2O$, crystallises in laminæ easily soluble in hot water.

*Lead hydrate* produces glycollic and diglycollic acids in about equal quantities.

*Mercuric oxide* differs in its action on monochloracetic acid from the preceding bases, producing not only glycollic and diglycollic acids, but also oxalic acid. Moreover, the mercuric glycollate formed in the reaction combines with the mercuric chloride produced at the same time to form a double salt, $(C_2H_3O_3)_2Hg.HgCl_2$, in which chlorine cannot be detected directly by means of silver nitrate.

*Silver oxide*, when boiled with monochloracetic acid, produces glycollic and a little oxalic acid. Silver glycollate crystallises in small laminæ free from water.

*Calcium Sulphhydrate* in excess, boiled with calcium monochloracetate, produces calcium thiodiglycollate, in accordance with the equation—

$$2C_2H_2ClCOOH + 2CaH_2S_2 = \begin{matrix} CH_2 \\ CH_2 \end{matrix} S \begin{matrix} COO \\ COO \end{matrix} Ca + CaCl_2 + 2H_2S.$$

J. R.

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**Remarkable Transformation of Normal Butyric Acid into Isobutyric Acid.** By E. ERLENMEYER (Liebig's Annalen, clxxxi, 126—128).

THE author has observed that a cold saturated solution of calcium butyrate, after being heated some 30 or 40 times in a sealed glass tube, became partially converted into isobutyrate, so that it no longer deposited crystals when heated. It was found that about one-tenth of the normal butyrate had been transformed into isobutyrate. The same result was not brought about by boiling a solution of normal calcium butyrate for 8 hours.

J. R.

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**On the Lactic Acid from Inosite.** By H. VOHL (Deut. Chem. Ges. Ber., ix, 984—987).

THE author showed many years ago that inosite, when fermented with putrid cheese or flesh, yields ordinary lactic acid. Hilger has since disputed this, stating that the substance thus produced is paralactic acid. Vohl has now made a fresh series of experiments on the subject, and has arrived at the same conclusion as before, namely, that the acid formed by the fermentation of inosite in contact with putrid cheese or flesh is ordinary lactic, and not paralactic acid.

J. R.

**Occurrence of Succinic Acid in Unripe Grapes.** By H. BRUNNER and R. BRANDENBURG (Deut. Chem. Ges. Ber., ix, 982—984).

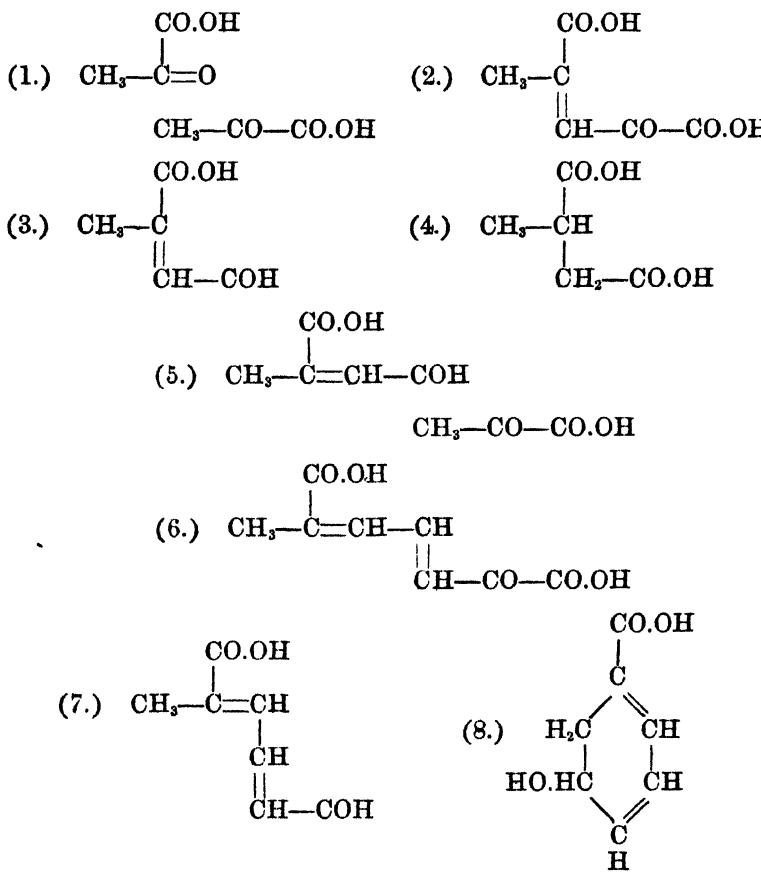
THE juice of grapes gathered in June, when neutralised with chalk, yields, amongst other products, a soluble lime-salt, crystallising in white hard crystals or in needles. The acid contained in the lime-salt, isolated by converting it into lead or silver salt and decomposing the latter with hydrogen sulphide, forms white crystals melting at 180° and subliming without decomposition. It gives with ferric chloride a pale brown, and with silver nitrate or lead acetate a white, amorphous precipitate. Its composition agrees with the formula $C_4H_6O_4$. The acid is, therefore, succinic acid.

J. R.

**The Condensations of Pyroracemic Acid.** By C. BÖTTINGER (Deut. Chem. Ges. Ber., ix, 836—843).

(*a.*) *Formation of Pyroracemic acid and Uvic acid.*—The experimental data relating to the formation of these acids from pyroracemic acid are to be found in vol. 172 *Liebig's Annalen*, in the *Deut. Chem. Ges. Ber.*, vi, 893, viii, 1583, ix, 670; also *Chem. Soc. J.*, 1873, p. 1221; 1874, p. 1158; 1876, p. 566. The decomposition process mentioned in the above was repeated, and in course of investigation of the volatile acids formed by this process, the author succeeded, by fractional crystallisation of their barium salts, in obtaining a substance soluble with difficulty. It was, however, found impossible to repeat the process so as to obtain more pure substance. The numbers obtained prove the substance to be barium uvate, $C_5H_6BaO_4 + 2\frac{1}{2}H_2O$. By treatment with hydrochloric acid, uvic acid was easily separated. Fusing point = 133°. Besides decomposing with barium hydrate, the effect of treatment with excess of sodium carbonate was next tried. The products obtained were of such a nature that their further investigation was deferred. By boiling the pyroracemic acid with ammonia, ammonium carbamate was formed, which separates in the neck of the retort as a crystalline incrustation. An examination of the other products proved that only small quantities of pyrotartaric acid were formed. Gaseous ammonia passed through pure pyroracemic acid causes such an evolution of heat that the liquid boils. A thick red fluid is formed, soon becoming acid, which dissolves in alcohol, and

is separated from this solution by ether. This product, and that arising from the action of glycocine on pyroracemic acid, whereby carbon dioxide is copiously evolved, and a considerable rise of temperature produced, have not been yet examined. An investigation in order to trace the possible connection between uvic and uvitic acids, did not result in establishing such connection. The following formulæ express a theoretical view of the formation of pyrotartaric and uvic acids :—



From these formulæ it will be observed that theoretically a molecule of pyroracemic acid decomposes, forming aldehyde and carbon dioxide, and the former, by a combined union and condensation with pyroracemic acid, gives rise to the formation of the higher acids.

The efforts of the author to obtain synthetically, compounds of pyroracemic acid with aldehyde were unavailing. He next investigated the possible influence of aldehyde added in the decomposition of the pyroracemic acid. This could be controlled in some degree by quantitative estimation of the products :—

10 grams of pyroracemic acid furnished 0·15 gram of uvic acid, and 1·2 grams of pyrotartaric acid.

10 grams of pyroracemic acid furnished, on addition of aldehyde, 0·34 gram of uvic acid, and 1·67 of pyrotartaric acid.

If fresh aldehyde be added from time to time, larger quantities of the bodies named are indeed formed, but they become very impure. It is considered, therefore, that the theoretical view proposed is the simplest, and best explains ascertained facts. Thus, it explains the formation of the non-volatile, uncrystallisable pyroracemic acid, which is probably, however, dipyroracemic acid, and might possibly be identical with hydruvic acid, $CH_3—C\begin{cases}OH\\CH_2—CO—CO.OH\\CO.OH\end{cases}$. All endeavours failed to obtain the acid $C_5H_6O_4$, by the introduction of iodine into the pyrotartaric acid molecule, with subsequent separation of hydriodic acid.

(*b.*) *Formation of Uvitic acid.*—By the decomposition of pyroracemic acid with excess of barium hydrate, Strecker and Finkh obtained oxalic acid, uvitic acid, and a syrupy acid which they called uvitoic acid (*Uvitonsäure*). The salts of this acid do not crystallise, and analyses thereof led to discordant results. On theoretical grounds they assumed its composition to be $C_9H_{12}O_7$. The author expresses the reaction by the following equation:—$6(C_3H_4O_3) = C_9H_8O_4 + 2(C_2H_2O_4) + 2\frac{1}{2}(C_2H_4O_2) + H_2O$.

The formation of uvitoic acid is here not taken into consideration. It was found that the syrupy acid named above is an impure substance, and analyses of its salts gave results quite different from those obtained by Strecker and Finkh. The author found acetic acid as a product of the decomposition, when pure pyroracemic acid was used, this Strecker and Finkh could not do, as they worked with a substance containing two-thirds of acetic acid. The formation of uvitic acid is regarded as due to the decomposition of a chain of four pyroracemic acid molecules, uvitoic acid being considered as an easily decomposible intermediate product, which wholly or partially splitting up, and acetic acid proportionately more or less occurring, confirms the view that the detached groups CO.OH and CO—CO.OH are not resolved into carbon dioxide, glycollic, and oxalic acids, but into carbon dioxide, acetic, and oxalic acids. By boiling barium pyroracemate with water, pyrotartaric, uvic, and uvitic acids are formed. Uvitoic acid is considered as a peculiar anhydride-like body, containing a uvitic acid residue. Further experiments have shown that uvitoic acid, if treated continuously with barium hydrate, is converted into uvitic acid; by mere exposure to the air it is also so converted. The decomposition products of pyroracemic acid are, therefore, carbon dioxide, acetic acid, oxalic and uvitic acids.

W. S.

**Oxypyrotartaric Acid, a derivative of Ethyl Aceto-acetate.** By E. DEMARÇAY (Compt. rend., lxxxii, 1337—1339).

WHEN ethyl aceto-acetate is heated on the water-bath with half its weight of anhydrous hydrocyanic acid for three hours, and the product thereby formed is afterwards heated with hydrochloric acid, the following reactions take place:—

$$\underset{\text{(Ethyl aceto-acetate).}}{CH_3—CO—CH_2—CO_2C_2H_5} + CNH = CH_3—\underset{\displaystyle CN}{\underset{|}{COH}}—CH_2—CO_2C_2H_5;$$

$$CH_3—\underset{\displaystyle CN}{\underset{|}{COH}}—CH_2—CO_2C_2H_5 + 3H_2O = CH_3—\underset{\displaystyle CO_2H}{\underset{|}{COH}}—CH_2—CO_2H$$
$$+ NH_3 + C_2H_6O.$$

The product is an oxypyrotartaric acid, which has not yet been obtained in the crystalline form. On neutralising it with baryta-water and boiling the aqueous solution of the salt thus formed, carbon dioxide is evolved, barium carbonate is deposited, and there remains a solution in which hydrochloric acid sets free an acid having all the properties of acetonic acid. This reaction is represented as follows:—

$$2\ \begin{array}{c} CH_3—COH—CH_2 \\ \quad\ \ | \qquad\ \ | \\ \quad CO_2 \quad CO_2 \\ \quad\ \ \diagdown\ \diagup \\ \qquad Ba \end{array} + H_2O = \left(\begin{array}{c} CH_3—COH—CH_3 \\ \quad\ \ | \\ \quad CO_2 \end{array}\right)_2Ba +$$
$$CO_2 + BaCO_3.$$

The oxypyrotartaric acid is decomposed by distillation, yielding water, citraconic anhydride, and a body having the properties of isopropyl alcohol. The formation of these products may be represented by the following equations:—

$$CH_3—\underset{\displaystyle CO_2H}{\underset{|}{COH}}—CH_2—CO_2H = \underset{\text{Isopropyl alcohol.}}{CH_3—CH.OH—CH_3} + 2CO_2;$$

$$CH_3—\underset{\displaystyle CO_2H}{\underset{|}{COH}}—CH_2—CO_2H = 2H_2O + \underset{\text{Citraconic anhydride.}}{\begin{array}{c} CH_3—C{=}CH \\ \quad\ \ | \qquad\ \ | \\ \quad CO \quad CO \\ \quad\ \ \diagdown\ \diagup \\ \qquad O \end{array}}$$

J. R.

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**The Structure and Formation of Organic Colouring Matters or Dye-stuffs.** By O. N. WITT (Deut. Chem. Ges. Ber., ix, 522—527).

WHILE neither benzene nor its nitro-, amido-, or hydroxy-derivatives are colouring matters, we find that the nitranilines and nitrophenols

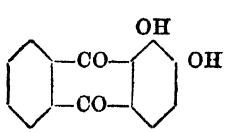
belong to that class; but they become colourless when acetyl is introduced into the former, or an alcohol-radical replaces in the latter the hydrogen of the hydroxyl. From this it follows that the colour of such bodies depends on the presence of a nitro-group and a group capable of forming salts. A compound requiring one of the latter group to become a colour may be called a *chromogen*, and the group which, when introduced into such a colourless body, imparts to it a colour, is a *chromophor*. Thus, nitrobenzene is the chromogen of nitraniline, and nitrophenol and nitroxyl their chromophors. The different nitrodiphenylamines are all acids and dye-stuffs, and their tinctorial power increases with the number of the nitroxyls.

Azobenzene, although a coloured body, is not a colouring matter, neither is benzidine, but by introducing the chromophor $-N{=}N-$, beautiful colours are produced. Amido- and oxyazobenzene are also dyes, and so is triamido-azobenzene (Manchester brown).

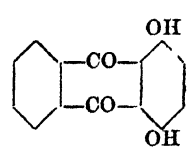
$C_6H_4[N{=}N.C_6H_3(NH_2)_2]_2$.—The corresponding body, $C_6H_4[N{=}N.C_6H_3(OH)_2]_2$, is a similar body, but has acid properties.

These free colouring matters are always less coloured than their salts. Thus, while the nitranilines, nitrophenols, picric acid, &c., are pale yellow, their salts are dark yellow, orange, or red, and the salts of yellow amidoazobenzene and oxyazobenzene are purple or orange-red. Nitroazobenzene is neutral and no dye-stuff, but azonitromethylphenyl is a yellow dye, because it is a derivative of the acid nitromethane.

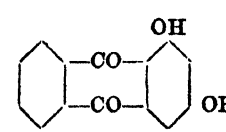
The coloured derivatives of anthraquinone show that the two groups CO can also act as a chromophor, if a salt-forming group is introduced; alizarin, purpurin, nltroalizarin, and diamido-anthraquinone are dye-stuffs; and their salts have a deeper colour than the free compounds. Of the many isomerides of alizarin, only quinizarin and xanthopurpurin are dye-stuffs; it seems, therefore, that such compounds must contain one hydroxyl in the ortho-position with regard to the chromophor:—



Alizarin.



Quinizarin.



Xanthopurpurin.

The chromogen of fluoresorcin is not known; it must be a colourless body, having the constitution $C_6H_4\left\langle\begin{array}{l}CO{-}C_6H_4\\ \quad\;\; | \\ \quad\;\; O \\ \quad\;\; | \\ CO{-}C_6H_4\end{array}\right.$, and may be called fluoresceogen. Its chromophor is O as well as phthalyl, $C_6H_4(CO)_2$, the latter is not sufficient, because phenolphthalein is no colouring matter. Fluorescein is a fugitive yellow colour, but its substitution-products dye fast colours, the most beautiful being the tetrabromo-compound or eosin. It appears from this, that of colouring matters having an analogous constitution, that forming the most stable salts is

the best colour, while in analogous bodies a change in the salt-forming groups does not much influence the shade :—

| | | | |
|---|---|---|---|
| Nitrophenol<br>Nitraniline | pale-yellow | Alizarin<br>Diamidanthraquinone | red or violet. |
| Picric acid<br>Trinitraniline | darker yellow | Rosaniline<br>Rosolic acid | red. |
| Amidazobenzene<br>Oxyazobenzene | yellow | Tetramidotetrazotriphenyl<br>Tetroxytetrazotriphenyl | brown. |

C. S.

## Reactions of α-Dinitrochlorobenzene. By WILLGERODT (Deut. Chem. Ges. Ber., ix, 977—982).

I. WHEN α-dinitrochlorobenzene is added to an alcoholic solution of aniline and hydrogen sulphide, a reaction takes place, resulting chiefly in the formation of the two following bodies, which are readily separated by taking advantage of their different degrees of solubility in alcohol.

1. The more soluble body is *α-dinitrophenylaniline*, $HN(C_6H_5)C_6H_3(NO_2)_2$. It crystallises, when pure, in long yellowish-red needles, which melt at 186°—187°.

2. The less soluble product forms a yellow powder melting at 272°—280°. Its composition agrees approximately with the formula $HS—C_6H_3(NO_2)_2$, which is that of α-dinitrophenyl-mercaptan. It has not been further investigated.

II. α-Dinitrochlorobenzene, when heated to 100°—130° with alcoholic ammonia in sealed tubes, yields *α-dinitrophenylamine*, $H_2N—C_6H_3(NO_2)_2$, melting at 182°—183°.

III. When α-dinitrochlorobenzene (1 mol.) is boiled with toluidine (2 mol.) dissolved in alcohol, the solution on cooling deposits reddish-yellow crystals of *α-dinitrophenyltoluidine* (orthoparanitrophenylparamidotoluene), melting at 137°. The mother-liquor of these crystals contains toluidine hydrochloride. Hence the reaction may be represented thus :—

$$2C_7H_9N + C_6H_3(NO_2)_2Cl = HN\begin{cases} C_7H_7 \\ C_6H_3(NO_2)_2 \end{cases} + H_2NC_7H_7.HCl.$$

α-Dinitrophenyltoluidine dissolves easily in alcohol, ether, and glacial acetic acid. It is very readily taken up by strong sulphuric acid, which, however, deposits the greater part on addition of water. It melts at 136°.

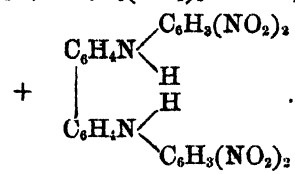
IV. When two molecules of α-dinitrochlorobenzene are boiled with three molecules or more of benzidine, the solution, on cooling, deposits brownish crystals of *mono-α-dinitrophenyl-benzidine*, (*mono-orthoparanitrophenyl-benzidine*). This is a neutral body, melting at 245°. Its formation is represented thus :—

$$3C_{12}H_8(NH_2)_2 + 2C_6H_3(NO_2)_2Cl = C_{12}H_8(NH_2)_2.2HCl$$

$$+ 2 \begin{cases} C_6H_4NH_2 \\ C_6H_4N\begin{cases} H \\ C_6H_3(NO_2)_2 \end{cases} \end{cases}.$$

But when equal numbers of molecules of *a*-dinitrochlorobenzene and benzidine are heated to 100°—150° with alcohol in sealed tubes for some hours, the chief product is *di-a-dinitrophenyl-benzidine* (*di-orthoparanitrophenyl-benzidine*), a yellow pulverulent substance melting above 330°, and dissolving sparingly in all ordinary solvents, but easily in strong sulphuric acid, with which it forms a fine violet solution. The formation of the body is represented by the equation—

$$2C_{12}H_8(NH_2)_2 + 2C_6H_3(NO_2)_2Cl = C_{12}H_8(NH_2)_2.2HCl$$



J. R.

## Dinitroparadibromobenzenes and their Derivatives.

By P. T. Austen (Deut. Chem. Ges. Ber., ix, 621—623).

Pure crystallised dibromobenzene, when heated with a mixture of strong sulphuric and fuming nitric acid, is converted into a mixture of *a*-, β-, and γ-dinitroparadibromobenzenes. The *a*-compound, which is the principal product, is obtained pure by crystallising the mixture repeatedly from carbon bisulphide, and finally from glacial acetic acid.

*a-Dinitroparadibromobenzene*, when pure, crystallises from glacial acetic acid in short white shining needles or small prisms, and from carbon bisulphide in small hard white crystals. It is insoluble in water, but easily soluble in hot absolute alcohol. Volatilises with water-vapour. Melts at 159°. Its composition agrees with the formula $C_6H_2Br_2(NO_2)_2$. The crystals, when heated to 100° with strong alcoholic ammonia in sealed tubes, are converted into

*Nitroparadibromaniline*, $C_6H_2Br_2(NO_2)NH_2$. This substance forms orange or red needles, which melt at 75°. It volatilises with water-vapour, and dissolves freely in most solvents. It reacts with amyl-nitrite at the ordinary temperature to form ordinary mononitroparadibromobenzene.

J. R.

## Synthesis of Symmetrical Ethyl-dimethyl-benzene.

By E. Wroblewsky (Deut. Chem. Ges. Ber., ix, 495—498).

Bromoxylidine in alcoholic solution, when treated with nitrous acid, yields a bromoxylene boiling at 204°, and remaining fluid at −20°. When a mixture of this bromoxylene and ethyl bromide is warmed with sodium, a reaction takes place, resulting in the formation of the hydrocarbon $C_6H_3(C_2H_5)(CH_3)_2$, which boils at 185°, is fluid at −20°, and has the sp. gr. 0·861. This substance yields mesitylenic and oxyuvitic acids by oxidation with dilute nitric acid.

J. R.

**Action of Ammonia on Chloracetylbenzene.** By W. STÄDEL and L. RÜGHEIMER (Deut. Chem. Ges. Ber., ix, 798).

IN their last paper, the authors state that the product of this reaction appears to be $C_6H_5.CO.CH_2.NH_2$; they have since found that it does not contain nitrogen, and is probably identical with Gräbe's benzoylcarbinol, $C_6H_5.CO.CH_2.OH$.

C. S.

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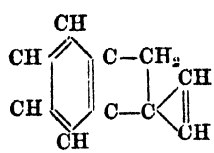
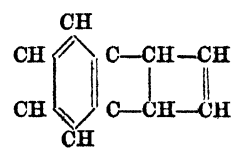
**On the Constitution of Naphthalene.** By F. WREDEN (Deut. Chem. Ges. Ber., ix, 590—592).

THE author proposes for naphthalene, instead of the symmetrical structural formula now adopted, the following formula (I), which he considers to be more in accordance with known facts. He believes also that an isomeric naphthalene is possible, the structure of which is represented by the formula II :—

I.



II.



J. R.

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**Benzylnaphthalene.**
By P. MIGUEL (Bull Soc. Chim. [2], xxv, 2—6).

THIS hydrocarbon is best prepared by heating in a large flask 140 parts of naphthalene, 20 parts of zinc-dust, and 100 parts of pure benzyl chloride. As soon as the reaction commences, the flask is put into tepid water, and when it is over the product is distilled in small retorts. First naphthalene passes over; the temperature rising gradually to 240°, and then rapidly to 310°, when benzylnaphthalene begins to distil as a yellowish oil, having a violet fluorescence, and solidifying quickly to a crystalline mass. When the distillation slackens, the receiver is changed, and now a red, fetid oil with a green fluorescence condenses, from which, on standing for some days, one-fourth of its weight of benzylnaphthalene crystallises out.

To purify the hydrocarbon, it is pressed out and redistilled, the portion boiling between 340°—350° being collected separately and allowed to crystallise very slowly from a mixture of alcohol and ether (or carbon sulphide). It forms monoclinic prisms, melting at 58·6°, and having at 17° the specific gravity 1·166, and boiling at 330°—340°. When pure it is quite odourless, but it generally retains a trace of naphthalene which may be removed by boiling it with water.

With chlorine it forms syrupy substitution-products, and on treating it with bromine in presence of carbon sulphide it yields a syrupy monobromide, $C_{17}H_{13}Br$, while by the direct action of bromine solid and very insoluble products are formed. Cold fuming nitric acid converts it into $C_{17}H_{11}(NO_2)_3$, which is a yellow, amorphous solid.

When the hydrocarbon is heated with a mixture of equal parts of common and of fuming sulphuric acid, the greater part dissolves, yielding benzylnaphthalenesulphonic acid, $C_{17}H_{14}SO_3$, which was obtained pure by decomposing the lead-salt with hydrogen sulphide. It does not crystallise; neither do its very soluble salts, except $C_{17}H_{13}SO_3K + H_2O$, which crystallises from alcohol in thin needles.

On fusing this salt with potash, a phenol is formed, which in the crude state forms a soft brown mass having a very disagreeable smell.

The hydrocarbon forms with picric acid a compound crystallising in yellow needles, which are decomposed at 100°.

C. S.

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## On two Naphthalene-disulphonic Acids and some Derivatives.

By R. EBERT and V. MERZ (Deut. Chem. Ges. Ber., ix, 592—612).

WHEN naphthalene is heated to 160°—180° with five times its weight of strong sulphuric acid, it dissolves therein easily and completely, forming two disulphonic acids (distinguished by the authors as $\alpha$- and $\beta$-acids), which may be separated by taking advantage of the difference in solubility of their calcium salts, the $\beta$-compound being much less soluble than the other, and not more soluble in boiling than in cold water. The calcium salts, when treated with potash or soda, yield the corresponding alkali salts.

*Naphthalene-disulphonic chlorides*, $C_{10}H_6\left\langle\begin{matrix}SO_2Cl\\SO_2Cl\end{matrix}\right.$. These bodies are formed by heating the potassium salts of the disulphonic acids to 140° with phosphorus pentachloride. The reaction is expressed by the equation—

$$C_{10}H_6\left\langle\begin{matrix}SO_2OK\\SO_2OK\end{matrix}\right. + 2PCl_5 = C_{10}H_6\left\langle\begin{matrix}SO_2Cl\\SO_2Cl\end{matrix}\right. + 2KCl + 2POCl_3.$$

The $\alpha$-compound crystallises in fine transparent, colourless, four- or six-sided plates. The crystals deposited from ether remain transparent, but those obtained from benzene turn opaque and porcelain-like, without altering in weight. The $\beta$-compound crystallises from hot saturated solutions in tufts of white needles. The two chlorides differ greatly in solubility, the former dissolving in 7·5 parts of benzene and easily in glacial acetic acid and ether, while the latter requires 221 parts of benzene, and dissolves only sparingly in the other liquids.

The $\alpha$-chloride melts at 157°—158°; the $\beta$-chloride at 226°. Both carbonise when heated, evolving sulphur dioxide. They are very slowly decomposed by water at the boiling heat, but more rapidly at 150° in sealed tubes, the products being hydrochloric acid and the respective disulphonic acids:—

$$C_{10}H_6(SO_2Cl)_2 + 2H_2O = C_{10}H_6(SO_2OH)_2 + 2HCl.$$

At 200° the disulphonic acids are resolved into sulphuric acid and naphthalene.

*Naphthalene-disulphamides*, $C_{10}H_6\begin{cases}SO_2NH_2\\SO_2NH_2\end{cases}$. These bodies are formed by triturating the disulphonic chlorides with ammonium carbonate and heating the mixture with strong ammonia. The $\alpha$-amide crystallises from hot saturated solutions in water or alcohol in silvery needles, which melt at 242°—343°. The $\beta$-amide crystallises best from boiling amyl alcohol in needles which remain unmelted at 305°.

*Naphthalene-disulphonic Acids*, $C_{10}H_6\begin{cases}SO_2OH\\SO_2OH\end{cases}$. The pure acids are best prepared by decomposing the respective chlorides with water at 150° (see above), or they may be obtained by decomposing their lead salts with hydrogen sulphide. The $\alpha$-acid crystallises from its aqueous solution in a vacuum in shining pointed needles: the $\beta$-acid forms small brilliant laminæ. Both acids are very freely soluble in water, and deliquesce in the air. Though dibasic, they yield only neutral salts, which are exceedingly stable, being decomposed only at a red heat. The salts of the $\alpha$-acid are much more soluble than those of the $\beta$-acid, and readily form supersaturated solutions. As a rule, the former crystallise much more easily than the latter. The author has analysed the potassium, sodium, calcium, barium, and lead salts of both acids, and in most cases determined their solubility in water.

*Dicyanonaphthalenes*, $C_{10}H_6\begin{cases}CN\\CN\end{cases}$. These bodies are obtained by distilling small quantities of the dry potassium salts of $\alpha$- and $\beta$-naphthalene-disulphonic acids with potassium cyanide. They closely resemble each other externally, and both sublime easily in long white needles. The $\alpha$-compound melts at 267°—268°; the $\beta$-compound at 296°—297°: the former is the more easily soluble. When heated to 200°—210° with hydrochloric acid, or when boiled with a solution of potash in amyl alcohol, they are converted into—

*Naphthalene-dicarbonic Acids*, $C_{10}H_6\begin{cases}CO_2H\\CO_2H\end{cases}$, in accordance with the following equation:—

$$C_{10}H_6(CN)_2 + 4H_2O = C_{10}H_6(CO_2H)_2 + 2NH_3.$$

These acids crystallise in needles, which are very sparingly soluble and melt only above 300°, with decomposition. They form neutral salts, which, with the exception of those of the alkalis, are very sparingly soluble, the salts of the $\alpha$-acid being, however, the more freely soluble. The potassium, calcium, and silver salts of both acids have been analysed. The free acids, when distilled with excess of calcium hydrate, are resolved into naphthalene and carbon dioxide.

*$\alpha$-Dioxynaphthalene and $\beta$-Naphthol-sulphonic Acid.*—The isomeric naphthalene-disulphonic acids behave differently on heating them with potash. The $\alpha$-acid, when heated to 250° with potassium hydrate and water, is converted into dioxynaphthalene. This body crystallises from benzene in long colourless needles, agreeing in composition with

the formula $C_{10}H_6(OH)_2$. It dissolves easily in hot water, ether, and alcohol. Alkaline and ethereal solutions blacken in the air. The pure substance melts at 186°, and sublimes at 160°—170°. Its aqueous solution is coloured dark-red by bleaching powder and by nitric acid.

β-Naphthalene-disulphonic acid, when heated with potash, is converted into β-naphthol-sulphonic acid, the potassium salt of which crystallises in long colourless needles or silvery laminæ, having the formula $C_{10}H_6(OH)SO_2OK$ + aq. The free acid, obtained by decomposing the lead salt with hydrogen sulphide, crystallises in white laminæ melting at 122°. It appears to be identical with Schäfer's naphtholsulphonic acid from β-naphthol. The potassium salt, when heated to 200° with hydrochloric acid, is resolved into β-naphthol and acid potassium sulphate.

J. R.

**Phenolmetasulphonic Acid.** By L. BARTH and C. SENHOFER (Deut. Chem. Ges. Ber., ix, 969—974).

THIS substance, which has not hitherto been known with certainty, is obtained by the authors as follows:—Metabenzene-disulphonic acid, dissolved in the smallest possible quantity of water, is heated to 170°—180° with two or three times its weight of potassium hydrate in a silver basin. The solution gradually becomes more and more concentrated until it acquires a thick pulpy consistence, at which stage the heating is stopped. The product is then dissolved in water, neutrallised with sulphuric acid, and evaporated, and the residue is exhausted with absolute alcohol, which takes up potassium phenolmetasulphonate, leaving potassium sulphate undissolved. The alcoholic solution, when evaporated, deposits crystals of the new salt, from which the free acid is obtained by adding to it the necessary quantity of sulphuric acid and a little water, evaporating to a syrup, agitating this with a mixture of alcohol and ether, filtering from potassium sulphate, and distilling with water. The acid thus obtained in aqueous solution is purified by converting it into lead-salt, decomposing the latter with hydrogen sulphide, and evaporating the liquid to a syrup, which gradually deposits the acid in delicate needles. The crystals dried in a vacuum contain 2 mols. of water: at 100°—112° they retain ½ mol., which is expelled at 140°. The acid gives a violet coloration with ferric chloride. Analysis agrees with the formula $C_6H_4(HO)SO_3H$.

The *potassium salt*, $C_6H_4(HO)SO_3K.H_2O$, crystallises in a mass of small needles, which melt at 200°—210°, and effloresce in the air. A basic potassium salt, obtained by dissolving the neutral salt and the necessary quantity of potash in alcohol, crystallises in silky needles. The *barium salt*, $(C_6H_5.HO.SO_3)_2Ba$, forms laminæ very easily soluble in water. The *copper salt*, $(C_6H_4.HO.SO_3)_2Cu + 6H_2O$, crystallises in large bright-green rhombic tables, very freely soluble in water. The dried salt is extremely hygroscopic, taking up water from calcium chloride. The *lead salt*, $(C_6H_4.HO.SO_3)_2Pb + 3H_2O$, forms colourless quadratic tables. The *silver salt* crystallises in delicate needles, which dissolve easily in water. The *ammonium salt* crystallises from strong solutions in fine needles, and from dilute solutions in tables: it is

freely soluble in water. The *sodium salt* crystallises with 1 mol. of water in large rhombic tables.

Potassium phenolmetasulphonate, when heated to 250° with potash, exchanges the group $SO_3H$ for HO, yielding resorcin free from hydroquinone or pyrocatechin. This behaviour of the meta-acid distinguishes it from the isomeric acids, neither of which yields resorcin when similarly treated.

The following table exhibits the differences observed by the authors in some of the salts of the three phenolsulphonic acids:—

| Salt. | Meta-acid (new). | Ortho-acid. | Para-acid. |
|---|---|---|---|
| K | Melts at 200°. Crystallises in masses of confused microscopic needles with 1 mol. water. | Melts at 240°. Crystallises in long flat needles, with 2 mol. water. | Does not melt at 260°. Crystallises in anhydrous hexagonal tables. |
| Ba | Small laminæ, composed of microscopic needles, containing ½ mol. water. | Indistinctly crystalline masses with 2 mol. water. Very soluble in water. | Long silky matted needles, containing 3 mol. water. |
| Pb | Crystallises in large rhombic tables, containing 3 mol. water. | Indistinct tables, with 1 mol. water. Dissolves with great difficulty in water. | Long needles grouped in nodules. Contains 2 mol. water. |
| Cu | Large thin bright green rhombic tables, containing 6 mol. water. | Pale-blue prisms. | Thick blue plates, resembling cupric sulphate. Contains 10 mol. water. |
| Na | Flat needles, or large rhombic tables, with 1 mol. water. | Indistinctly crystalline masses, containing 1½ mol. water. | Prismatic crystals, containing 2 mol. water. |

J. R.

**Action of Ethyl Nitrate on Benzoic Acid in presence of Concentrated Sulphuric Acid.** By F. FITTICA (Deut. Chem. Ges. Ber., ix, 794—795).

WHEN a solution of equal numbers of molecules of benzoic acid and ethyl nitrate in pure ether is added to concentrated sulphuric acid, at a temperature not exceeding 75°, a little metanitrobenzoic acid is formed, together with a large quantity of ethyl benzoate and a liquid boiling at 270°—280°. The latter was decomposed by potash, and thus an acid obtained, melting at 136°—137°, and consisting of a compound of benzoic acid and the nitrobenzoic acid, melting at 128°—130°.

C. S.

## Nitrobenzoic Acids. By F. FITTICA (Deut. Chem. Ges. Ber., ix, 788—794).

THE author formerly described a fourth nitrobenzoic acid melting at 127°, which is converted into common nitrobenzoic acid, melting at 142°, by preparing the ethylic ether and decomposing the latter with potash. The new acid is formed only by using a nitric acid of no higher specific gravity than 1·42, which is mixed with the same quantity of sulphuric acid. The nitration must take place at a temperature not exceeding 60°, and in the purification no caustic baryta must be used. If these conditions are not attended to, only common nitrobenzoic acid is produced. The nitro-acid thus obtained did not melt at 127°, but at 135°—136°, but yet the author believes it to be a new isomeride, because the corresponding amido-acid differs from common or metamidobenzoic acid.

The amido-acid is obtained by the action of tin and hydrochloric acid at a temperature not exceeding 60°, or by dissolving the nitro-acid in an *excess* of cold dilute ammonia, and saturating the liquid with hydrogen sulphide at 70°—80°. It melts at 154°—156°, or at 156°—158°, is almost tasteless, and less soluble in water than the meta-acid, which has an intensely sweet taste. Its lead-salt is a heavy yellow powder, dissolving in 400 parts of hot water, while lead metamidobenzoate is readily soluble in hot water, and crystallises in colourless needles.

The sulphate of the new amido-acid crystallises in thick, short, yellowish prisms, melting at 225°, while that of the meta-compound forms thin, silky, white needles, melting at 235°, and being more freely soluble.

When the new nitro-acid is reduced by hydrogen sulphide, in the form of the normal ammonium-salt, a compound of the amido- and nitro-acid $C_6H_4(NH_2)CO_2H + C_6H_4(NO_2)CO_2H$ is formed, separating from hot water in yellowish indistinct crystals, which concentrated sulphuric acid resolves into its constituents.

C. S.

## Sulphoparachlorobenzoic Acid. By THEODOR CÖLLEN (Deut. Chem. Ges. Ber., ix, 758—760).

THIS acid was prepared by passing the vapour of sulphuric anhydride into parachlorobenzoic acid dried at 100°, and finely triturated; or by mixing parachlorobenzoic acid with fuming sulphuric acid at the ordinary temperature, and promoting the reaction by gently warming the mixture. Its formation was accompanied by that of a small quantity of an isomeric acid, from which it was separated by crystallisation of the lead salts.

Sulphoparachlorobenzoic acid crystallises from its aqueous solution in white needles containing 3 mol. of water. When heated it yields a sublimate of parachlorobenzoic acid. The *lead salt* crystallises in rhombic tables, with 4 mol. of water; its hot aqueous solution readily deposits a basic salt. The *barium salt* forms tabular crystals, with 3 mol. of water. The *copper salt* is deposited in long blue needles,

containing 6 mols. of water, and deliquescing in the air. The neutral *potassium salt* forms crystals resembling quartz: the acid salt crystallises in needles.

J. R.

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**Miscellaneous Notes.** By C. BÖTTINGER (Deut. Chem. Ges. Ber., ix, 802—804).

SULPHOPARABROMOBENZOIC acid yields a chloride, melting at 155°, with decomposition; by the action of zinc-dust on its alcoholic solution no sulphobenzoic acid is formed, but one containing both sulphur and bromine, which seems to be formed by a reaction analogous to Zincke's.

By the action of hydrogen sulphide on pyroracemic acid, a thiolactic acid, $CH_3.CH(SH).CO_2H$ is formed.

C. S.

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**Decomposition of Oxethylcarbimidamidobenzoic Acid by Nitrous Acid.** By P. GRIESS (Deut. Chem. Ger. Ber., ix, 796—798).

THIS compound, which is obtained by the action of cyanogen on an alcoholic solution of metamidobenzoic acid, has the constitution $C_6H_4.NH\left\{\begin{matrix}COOH\\C(NH)OC_2H_5\end{matrix}\right.$. When treated in hydrochloric acid solution with nitrous acid it yields the body $C_{10}H_{11}NO_4$, crystallising from hot water in soft, glistening plates melting at 189°. This body is an acid. The barium salt, $(C_{10}H_{10}NO_4)_2Ba + 2H_2O$, forms white, indistinct crystals; the silver salt, $C_{10}H_{10}NO_4Ag$, is a white crystalline precipitate. When the acid is boiled with baryta-water, it takes up water and yields amidobenzoic acid, carbon dioxide, and alcohol. It belongs therefore to the class of urethanes, and is consequently also formed by the action of chlorocarbonic ether on amidobenzoic acid. Its formation from oxethylcar bimidamidobenzoic acid is explained as follows:—

$$C_6H_4.NH\left\{\begin{matrix}COOH\\C(NH)OC_2H_5\end{matrix}\right. + HNO_2 = C_6H_4.NH\left\{\begin{matrix}COOH\\CO.OC_2H_5\end{matrix}\right. + N_2 + H_2O.$$

C. S.

**On β-Benzhydrylbenzoic Anhydride and β-Benzylbenzoic Acid.** By F. ROTERING and TH. ZINCKE (Deut. Chem. Ges. Ber., ix, 631—633).

β-BENZOYLBENZOIC acid, $C_6H_5—CO—C_6H_4—CO_2H$, behaves towards reducing agents in the same manner as the α-acid, the group CO being transformed into CH.OH; but the acid thus formed is not stable, and breaks up at the moment of its formation into water and an anhydride—

$$\begin{matrix}C_6H_5—CH—C_6H_4\\ \quad\;\;|\\ \quad\;\;O—CO\end{matrix}$$

This body crystalises from hot alcohol or ether in colourless prisms and from dilute acetic acid in laminæ, which melt at 115° and sublime at a higher temperature. By oxidation with potassium bichromate and sulphuric acid it is re-converted into β-benzoylbenzoic acid. It is remarkably indifferent towards bases, being dissolved only slowly by caustic alkalis and their carbonates and not at all affected by ammonia. When heated to 140° with phosphorous pentachloride, it yields anthraquinone and chlorinated derivatives thereof.

By the prolonged action of sodium amalgam on β-benzoylbenzoic acid the reducing action is carried further, resulting in the formation of *β-benzylbenzoic acid*, $C_6H_5—CH_2—C_6H_4—COOH$, which crystallises from weak spirit in brilliant needles, melting at 114° and subliming without decomposition at a higher temperature. The barium and calcium salts of this acid are crystalline, the silver salt is amorphous. The methyl-ether, $C_{14}H_{11}O_2CH_3$, is a thick, colourless liquid, soluble in alcohol and ether.

J. R.

**Rosolic Acid.** By C. LIEBERMANN and F. SCHWARZER (Deut. Chem. Ges. Ber., ix, 800—802).

ROSOLIC acid is readily formed by adding 1 part of sulphuric acid diluted with one-third of its weight of glacial acetic acid to a mixture of 1 part of phenol and 2·5 parts of salicylaldehyde, and heating the mixture on a water-bath after the rather violent action is over. It was purified by converting it into the magnesium-salt as well as into Dale and Schorlemmer's sodium-sulphide compound. Its formation is easily explained—

$$C_6H_6O + 2C_7H_6O_2 = C_{20}H_{14}O_3 + 2H_2O.$$

When salicylaldehyde is treated with sulphuric acid without the presence of phenol, a different red colouring matter is obtained, which dissolves in alkalis with a more purplish-red colour and forms a more soluble magnesium-salt.

C. S.

**Derivatives of Uvitic Acid.** By C. BÖTTINGER (Deut. Chem. Ges. Ber., ix, 804—810).

THIS acid, heated with a mixture of nitric acid and sulphuric acid, yields, besides other products, two mononitro-compounds.

*α-Mononitrouvitic acid* is the chief product; it dissolves but very sparingly in cold water and a little more freely in boiling water, and crystallises in groups of needles or single-pointed prisms, melting at 226°—227° and containing 2 mols. of water.

*β-Mononitrouvitic acid* is much more freely soluble in water, and forms acute rhombohedrons, melting at 249°—250 and containing half a mol. of water.

The potassium-salt of the α-acid is very soluble and forms microscopic needles containing 1 mol. of water. The barium-salt dissolves but sparingly in hot water and forms slender needles, which lose 1 mol.

of water at 150°. The calcium-salt, which is more soluble, crystallises in needles with 3 mols. of water.

The two nitro-acids were treated with tin and hydrochloric acid, and thus the amido-acids obtained.

*α-Amidouvitic acid* is insoluble in water and sparingly soluble in hot alcohol, from which it crystallises in small yellow needles, melting and decomposing at 240°. Its impure alcoholic solution shows a splendid greenish-blue fluorescence, but that of the pure acid is less beautiful and of a reddish-blue. *β-monamidouvitic acid* possesses very similar properties and melts under decomposition at 250°—255°.

When the α-acid is submitted to the diazo-reaction, it is converted into *α-oxyuvitic acid*, which is identical with that which Oppenheim and Pfaff obtained by the action of chloroform on sodacetic ether. The β-acid yields an oxyacid crystallising from hot water in long, brittle needles, which decompose at 220°, giving off the smell of phenol.

C. S.

## A Double Salt of Quinic and Acetic Acids.

By E. GUNDELACH (Bull. Soc. Chim. [2], xxv, 500).

THE salt originally obtained was quinate and acetate of calcium, which was found in some commercial quinate of calcium. The double salt may be prepared by mixing solutions of quinate and acetate of calcium in molecular proportions, and evaporating the liquid until a crust begins to form upon the sides of the containing vessel. In a day or two the whole becomes crystalline. The salt is stable and may be purified by crystallisation. Its formula is—

$$C_7H_{11}O_6—Ca—C_2H_3O_2 + H_2O.$$

This water is not lost at 150°, above which temperature the salt decomposes.

If from a solution of the salt the lime be removed by oxalic acid, and the liquid be concentrated, acetic acid is evolved and quinic acid crystallises out.

C. H. P.

## Formation of Azo-compounds. By ANTON FLEISCHER (Deut. Chem. Ges. Ber., ix, 992).

DIPHENYLSULPHOCARBAMIDE, when added in small quantities to fuming nitric acid, is violently acted on. The resulting red liquid, when poured into water, deposits a considerable quantity of a yellow nitro-compound, which after drying is partly soluble and partly insoluble in alcohol. The insoluble portion dissolves easily in strong nitric acid, forming a solution which, on standing, deposits small yellow crystals very sparingly soluble in water. Analysis of this substance shows it to be tetranitrazoxybenzene, $C_{12}H_6(NO_2)_4N_2O$.

Diphenylsulphocarbamide dissolves in strong sulphuric acid, with slight rise of temperature. The solution, when heated, evolves gases containing sulphur dioxide and oxysulphide, and on pouring the

resulting mass into water and allowing it to stand for two days, it becomes converted into a magma of crystals, probably of amidobenzenesulphonic acid. But when the mass, after dilution with water, is at once neutralised with potash, aniline separates out. Most probably the reaction consists primarily in the formation of sulphanilic acid, which, when neutralised, breaks up thus:—

$$C_6H_5HN—SO_3H + KOH = KHSO_4 + C_6H_5NH_2.$$

The formation of amidobenzenesulphonic acid in the above reaction is therefore preceded by the formation of sulphanilic acid, which on prolonged standing under water is resolved into aniline and sulphuric acid; and these products further react to form amidobenzenesulphonic acid.

J. R.

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## Phenolbidiazobenzene and Analogous Compounds.

By PETER GRIESS (Deut. Chem. Ges. Ber., ix, 627—630).

THE author has previously shown (*Phil. Trans.*, 1864, 688) that diazobenzene nitrate, when mixed with moist barium carbonate, is converted into phenoldiazobenzene and phenolbidiazobenzene, the formation of these bodies being due, as he supposed, to the combination of the phenol first formed in the decomposition with diazobenzene, thus:—

$$\underset{\text{Diazobenzene.}}{C_6H_4N_2} + \underset{\text{Phenol.}}{C_6H_6O} = \underset{\text{Phenoldiazobenzene.}}{C_{12}H_{10}N_2O};$$

$$2(C_6H_4N_2) + C_6H_6O = \underset{\text{Phenolbidiazobenzene}}{C_{18}H_{14}N_4O}.$$

The correctness of this view, as regards the former compound, was confirmed by Kekulé and Heidegh, who obtained it by the action of diazobenzene nitrate on phenol-potassium; and the author has found that the latter compound is formed with equal facility when a solution of phenoldiazobenzene in potash is mixed with aqueous diazobenzene nitrate:

$$C_{12}H_{10}N_2O + C_6H_4N_2 = C_{18}H_{14}N_4O.$$

*Phenoldiazobenzenediazotoluene*, $C_{19}H_{16}N_4O$, is likewise readily formed on mixing a solution of phenoldiazobenzene in potash with an equal number of molecules of diazotoluene nitrate. The resulting precipitate, purified by crystallization from alcohol, forms small yellowish warty masses, which melt at 110°. In physical characters it closely resembles phenolbidiazobenzene.

To this class of compounds belong also oxybenzodiazobenzoic acid, $C_{14}H_{10}N_2O_5$, and oxybenzobidiazobenzoic acid, $C_{21}H_{14}N_4O_7$, two products of the decomposition of diazobenzoic acid formerly described by the author. They are readily formed by synthesis, the former by mixing a solution of oxybenzoic acid in potash with an aqueous solution of sulphodiazobenzoic acid, and adding hydrochloric acid, and the latter by the action of sulphodiazobenzoic acid on an alcoholic solution of the former.

J. R.

**Azo-derivatives of Diphenyl.** By H. WALD (Deut. Chem. Ges. Ber., ix 847).

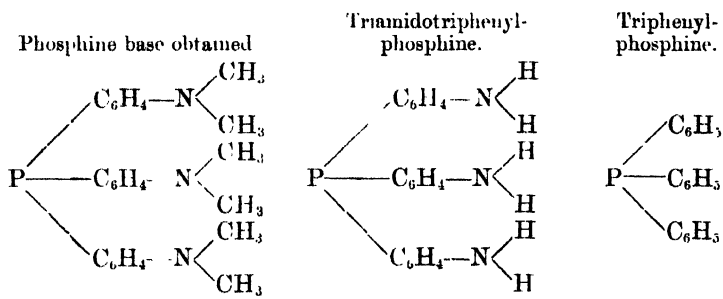
BY the action of sodium amalgam on para-nitro-diphenyl a beautiful brick-red reduction-product was obtained, which is insoluble in ordinary solvents, but may be recrystallised from hot aniline, and dissolves in concentrated sulphuric acid to which it communicates an intense red colour.

W. S.

**Action of Phosphorus Trichloride on Dimethyl-aniline.** By J. HANIMANN (Deut. Chem. Ges. Ber., ix, 845).

WHEN phosphorus trichloride and dimethyl-aniline are heated for some hours to 160°, methyl chloride is abundantly formed, and the aqueous solution of the residue furnishes with sodium hydrate solution a semi-solid precipitate, which contains much dimethyl-aniline. The latter can be removed by boiling with water. The residue recrystallised from alcohol furnishes a crystalline white basic body, which appears to be $P'''\left(C_6H_4—N\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right.\right)_3$.

On heating with fuming hydrochloric acid to above 160°, this body splits up into methyl chloride. It is probable that by completely depriving it of methyl by the above treatment, triamido-triphenyl-phosphine would be formed, from which triphenyl-phosphine might be prepared. The quantity of the compound actually obtained is but small.




W. S.

**Dibenzamide.** By L. BARTH and C. SENHOFER (Deut. Chem. Ges. Ber., ix, 975—977).

THIS hitherto unknown derivative of benzoic acid has been obtained by the authors by the action of a mixture of sulphuric acid and phosphoric anhydride on cyanobenzene. It is best prepared as follows:—Cyanobenzene (7 parts) is slowly added to a mixture of oil of vitriol (7 parts) and phosphoric anhydride (4 parts) and agitated therewith till the whole becomes homogeneous. After standing for some hours, water is added and the solution left to itself, whereupon it deposits a mass of fine needles, which after crystallisation from weak spirit, consist of pure

dibenzamide. The product forms long thin colourless needles, which melt at 144° and decompose without subliming at a higher temperature. It dissolves sparingly in boiling water, easily in alcohol, ether, chloroform, and benzene. Its reaction is neutral. Analysis agrees with the formula $C_{14}H_{11}NO_2$. The formation of the body may be thus represented:

$$2(C_6H_5.CN) + 2H_2O = (C_7H_5O)_2.NH + NH_3.$$

Dibenzamide boiled with potash-ley yields ammonia and potassium benzoate. When agitated with dilute soda ley in the cold it forms *sodium-dibenzamide*, $(C_7H_5O)_2NNa$, which crystallises from water in short prisms containing $\frac{1}{2}$ mol. of water. The aqueous solution of sodium-dibenzamide gives precipitates with salts of the heavy metals. The *silver compound* is a white semi-crystalline body. The *mercury, zinc, lead, and copper compounds* are curdy precipitates, quickly becoming crystalline.

J. R.

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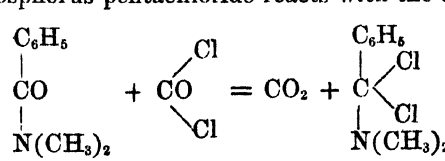
**Diethyl- and Dimethyl-Benzamide.** By F. HALLMANN (Deut. Chem. Ges. Ber., ix, 846).

DIETHYLAMINE or dimethylamine completely freed from water, are treated with benzoyl chloride. On account of the energetic action taking place, however, the precaution is taken to dilute both the chloride and the bases with eight times their volume of ether. The hydrochlorides are extracted with water, and the ethereal solution is dried over calcium chloride and evaporated.

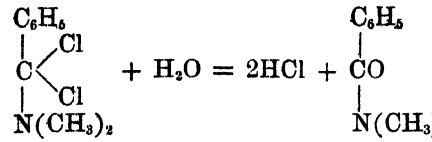
*Diethyl-benzamide* is a colourless oil, boiling at 280° to 282°. It is not miscible with water, is soluble in dilute hydrochloric acid, but is reprecipitated on addition of water.

*Dimethyl-benzamide* crystallises, the crystals being easily soluble in water, melting from 41° to 42°, and boiling from 255°—257° (uncorrected). Heated with hydrochloric acid to 200°, the amide separates into dimethylammonium chloride and benzoic acid.

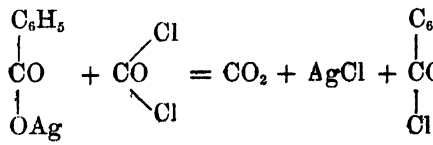
On enclosing in a sealed tube equal volumes of liquid carbonyl chloride and dimethyl-benzamide, and leaving the mixture to stand over night, a solid white crystalline mass was found in the tube, and on opening, streams of pure carbon dioxide escaped. The crystals fumed in damp air, smelt like benzoyl chloride, and in presence of water decomposed readily, yielding hydrochloric acid and dimethyl-benzamide. Thus, phosgene acts on this amide exactly as, according to Wallach's researches, phosphorus pentachloride reacts with the amides:—



*Dimethylbenzamido-chloride.*—This body, which is a representative of the class, amido-chlorides (Wallach), forms white, deliquescent crystals, melting-point, 36°. It is decomposed in presence of moisture, thus:—



The method given for preparing this amido-chloride is considered of practical interest, as the substance is furnished pure, only carbonic oxide being formed besides, and escaping, whereas when phosphorus pentachloride is used, the oxychloride remains. V. Meyer has already shown that the action of phosgene on silver benzoate exactly expresses the mode of action of phosphorus pentachloride on the benzoates, thus :—



W. S.

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**Reactions of Carbodiphenylimide.** By W. WEITH (Deut. Chem. Ges. Ber., ix, 810—820).

WHEN carbodiphenylimide is heated with diphenylthio-urea to 150°, phenylthiocarbimide and $\alpha$-triphenylguanidine are formed :

$$C(NC_6H_5)_2 + CS(NH.C_6H_5)_2 = CS.NC_6H_5 + C(NC_6H_5)(NH.C_6H_5)_2.$$

The same reaction takes place when a solution of carbodiphenylimide in benzene is heated on a water-bath with an alcoholic solution of the thio-urea and the theoretical quantity of hydrochloric acid; the presence of the acid facilitating the formation of the strongly alkaline guanidine.

These reactions explain the action of iodine on disubstituted thio-ureas, which Hofmann discovered, and which takes place in the following way :—

$$(1.)\quad CS(NH.C_6H_5)_2 + I_2 = C(NC_6H_5)_2 + S + 2HI.$$

The diphenylcarbimide is then further acted upon by an excess of the thio-urea as above; at the same time some of the diphenylcarbimide takes up water and is transformed into diphenylurea.

When an alcoholic solution of equal molecules of diparatolylthio-urea, carbodiphenylimide and hydrochloric acid is boiled for an hour, it yields paratolylthiocarbimide and a tolylphenylguanidine.

On heating a mixture of diphenyl-urea and carbodiphenylcarbimide, phenyl cyanate distils over, and $\alpha$-triphenylguanidine is left behind; this reaction takes place more readily in presence of hydrochloric acid. The same products are obtained by heating diphenyl-urea with phosphorus trichloride to 145°—150°, which reaction is quite analogous to the action of iodine on the thio-urea.

When hydrogen sulphide is passed into a solution of cyananilide, monophenyl-thiourea is formed:

$$CN(NH.C_6H_5) + H_2S + CS\left\{\begin{matrix} NH_2 \\ NH.C_6H_5 \end{matrix}\right.$$

C. S.

**Phosphenyl Bromide and Derivatives.** By A. MICHAELIS and H. KÖHLER (Deut. Chem. Ges. Ber., ix, 519—521).

WHEN dry hydrobromic acid is passed into boiling phosphenyl chloride, hydrochloric acid is given off, and some benzene, diphenyl, free phosphorus and its bromide and chloride are formed, besides *phosphenyl bromide*, $C_6H_5PBr_2$, which is a colourless liquid, soon turning yellow, and depositing a red body in sunshine. It boils at 255°—257°. Water decomposes it into hydrobromic acid, phosphenylic acid, and a little phenylphosphine. The formation of the bye-products of phosphenyl bromide may be explained by the following equations:—

$$C_6H_5PCl_2 + HBr = C_6H_6 + PCl_2Br.$$
$$3PCl_2Br = 2PCl_3 + PBr_3.$$
$$C_6H_5PCl_2 + HBr = C_6H_5Br + PCl_2H.$$
$$3PCl_2H = PH_3 + 2PCl_3.$$
$$PH_3 + PCl_3 = P_2 + 3HCl.$$

Phosphenyl bromide is also formed by the action of phosphorus tribromide on mercury-diphenyl. Bromine readily combines with the dibromide to tetrabromide, $C_6H_5PBr_4$ forming a dry, reddish-yellow mass. It becomes darker on heating, melts at 207°, and sublimes in needles, which are grouped in stars. It fumes in the air, and water decomposes it violently:

$$C_6H_5PBr_4 + 3H_2O = C_6H_5PO(OH)_2 + 4HBr.$$

The tetrabromide can take up another molecule of bromine, forming $C_6H_5PBr_6$, which above 110° sublimes in dark red prismatic needles.

C. S.

**Hesperidin.** By E. HOFFMANN (Deut. Chem. Ges. Ber., ix, 685—690).

THIS glucoside is resolved by dilute acids into glucose and *hesperetin*:

$$C_{22}H_{26}O_{12} = C_6H_{12}O_6 + C_{16}H_{14}O_6.$$

The latter compound forms white crystals, melting at 223°, and having an intensely sweet taste. It is almost insoluble in cold water, but dissolves readily in alcohol and ether, and gives with ferric chloride a deep brownish-red colour. Caustic potash resolves it at 100° into phloroglucin and *hesperitic acid*:

$$O\left\{\begin{matrix} C_6H_5O_2 \\ C_{10}H_9O_3 \end{matrix}\right. + H_2O = C_6H_6O_3 + C_{10}H_{10}O_4.$$

This acid melts at 225°, but sublimes already at 223°, a small portion being decomposed, with the formation of a body resembling vanillin. When the acid is fused with potash, it yields protocatechuic acid and acetic acid.

An aqueous solution of the free acid gives no reaction with ferric chloride, which gives with its neutral salts a cinnamon-brown precipitate.

C. S.

## Aurantiin and Murrayin. By E. HOFFMANN (Deut. Chem. Ges. Ber., ix, 690—693).

DE VRIJ found in the flowers of *Citrus decumana* a glucoside, which he believed to be hesperidin, but it is quite a different body, which may be called *aurantiin*. It crystallises in small, yellow, monoclinic prisms, dissolving freely in hot and 300 parts of cold water, and melting at 171°. The crystals consist of $C_{23}H_{26}O_{12} + 4H_2O$, and lose their water at 100°; they have an intensely bitter taste, and give with ferric chloride a deep, brownish-red colour. When fused with potash, it yields a product, giving with ferric chloride a green colour, which, however, is not due to protocatechuic acid.

De Vrij's *murrayin*, $C_{18}H_{12}O_{10}$, which he found in the flowers of *Murraya exotica*, is also a glucoside, which melts at 170°, and gives with ferric chloride a bluish-green colour.

C. S.

## The Milky Juice of Plumieria Acutifolia and Plumieric Acid. By C. A. OUDEMANS (Liebig's Annalen, clxxxi, 154—175).

THIS shrub, which belongs to the family of the Apocyneæ, is largely grown, chiefly in grave-yards in Java and the other Sunda islands. It contains a milky juice, in which Altheer found three new acids, which he called α-, β-, and γ-plumieric acids. In the old fermented juice he also found volatile fatty acids.

The material which the author examined was collected by Dr. de Vrij, who evaporated the fresh juice to dryness at 100°, and obtained thus 30·5 per cent. residue, which consisted chiefly of an organic calcium salt, a kind of caoutchouc and of resins.

To isolate the calcium salt, the substance was exhausted with petroleum-naphtha and the residue heated with dilute acetic acid, which dissolved the salt, while parts of the plant and a humus-like mass remained behind. On concentrating the solution, calcium-salts of different forms separate out, which, however, all contain the same acid for which the name *plumieric acid* is retained. It has the formula $C_{10}H_{10}O_5$, and forms four series of salts, from which it appears that it contains one carboxyl and three hydroxyls. It is obtained by converting the calcium-salt into potassium plumierate, decomposing the latter with sulphuric acid, and extracting the solution with ether.

It is readily soluble in alcohol and freely but slowly in ether. In cold water it dissolves but very sparingly, and from a hot solution it separates in microscopic crystals, or on slow evaporation in indistinct

crusts. It melts at 139°, and decomposes a few degrees above, $C_{10}H_6K_4O_5 + 3H_2O$ forms monoclinic crystals, $\infty P$, $\infty \bar{P} \infty$ and $0P$, and is very soluble and deliquescent. On dissolving the acid in ammonia and evaporating the solution under an exsiccator, crystals of a deliquescent salt are frequently formed, which give, with silver nitrate, a precipitate containing 3 atoms of silver. On standing longer, the crystals disappear, and an amorphous residue is obtained, which is readily soluble and gives a silver-salt containing two atoms of the metal. $(C_{10}H_9O_5)_2Ca + 4H_2O$ is obtained by dissolving equal mols. of the acid and the dicalcic salt in water and evaporating, when the salt crystallises in small hexagonal pinacoïds. It dissolves at 20° in 200 parts of water, but much more freely in boiling water. $C_{10}H_8CaO_5 + 5H_2O$ exists in the juice of the plant, and forms rhombic crystals, showing the faces $\infty P$, $\infty \bar{P} \infty$, $\breve{P} \infty$ in $0P$. One part dissolves at 20° in 400 parts of water; in boiling water it is a little more freely soluble, easily forming supersaturated solutions. $(C_{10}H_7O_5)_2Ca_3 + 4H_2O$, was obtained in small thick prisms by adding lime-water to a hot solution of the last salt. A salt with 5 mols. of water was once obtained by exhausting the crude calcium-salt with hot water.

$C_{10}H_8Ag_2O_5 + H_2O$ is a white crystalline precipitate; $C_{10}H_7Ag_3O_5 + 1\frac{1}{2}H_2O$, is a similar body crystallising from hot water in needles.

When plumieric acid is oxidised by a dilute solution of chromic acid it is resolved into formic acid (or carbon dioxide), and the acid, $C_9H_8O_4$, which is very sparingly soluble in water. $C_9H_5Ag_3O_4$, separates from a warm solution in fibrous crystals.

When plumieric acid is heated with water and sodium amalgam on a water-bath, it combines slowly with hydrogen to *hydroplumieric acid*, $C_{10}H_{12}O_5$, which, on evaporation of its ethereal solution, separates as a varnish, becoming crystalline on standing, and freely soluble in water.

When plumieric acid is heated above its melting point, it gives off first water and acetic acid, then an oil having the odour of cinnamaldehyde distils over, and a small quantity of a crystalline substance sublimes. When the oil is oxidised, a crystalline acid is formed. On melting plumieric acid with potash, an acid is formed, giving the characteristic reactions of salicylic acid. Plumieric acid is most probably an oxymethyldioxycinnamic acid:—

$$C_6H_2\left\{\begin{array}{l} CH_2.OH \\ C_2H_2.CO_2H. \\ (OH)_2 \end{array}\right.$$

C. S.

## Contributions to the Knowledge of Elemi. On Amyrin.

By E. Buri (N. Rep. Pharm., xxv, 193—204).

Flückiger mentioned, in his last reports on the chemistry of elemi, that bryoïdin, of the formula $(C_{10}H_{16})_2 + 3H_2O$, constituted only a very small proportion of the crystallisable matter present in the resin, and assumed that the greater part consisted of amyrin of the formula $(C_{10}H_{16})_2 + H_2O$, which body the author has more fully investigated.

*Preparation.*—Amyrin is found in elemi in the form of microscopic prisms, which can be separated from the other ingredients by treatment with cold alcohol, the former being insoluble in that liquid. By repeatedly recrystallising the residue from hot alcohol, amyrin is obtained in colourless needles, joined together as globular aggregates of silky lustre. It melts at 177°, but re-solidifies at a much lower temperature. Water does not dissolve it, but ether, chloroform, and carbon bisulphide dissolve it easily. Experiments have shown that 100 parts of alcohol dissolve 3·627 parts of amyrin at 16°. Concentrated sulphuric acid dissolves amyrin with a reddish colour. It is not attacked by melting potash.

*Optical Investigation.*—The rotation in a layer 200 mm. long was equal to + 4·5° at 16°. Sp. gr. of the solution at 16° = 0·8255 (sodium light. Wild's instrument).

Amyrin, when heated in a retort, melts and decomposes, giving at 200° a yellow, thin, oily distillate, which turns thicker as the temperature rises. The distillate afterwards solidifies, and at the end, yellow clouds ascend, which condense in the neck of the retort to a yellow powder, leaving behind a shiny blistered coke. On heating a thin layer very carefully, amyrin sublimes in long thin needles, but the yield is only very small. Amyrin dried at 100° gave, by analysis, 83·31 to 83·77 p.c. carbon, and 11·39 to 11·81 hydrogen, agreeing nearly with the formula $C_{25}H_{42}O$, which requires 83·80 C., 11·73 H, and 4·47 O.

*Acetyl-amyrin.*—Amyrin was heated with about four times its quantity of acetic anhydride in a sealed tube to 150° for several hours, and the residue dissolved in hot alcohol and recrystallised, when acetyl amyrin was obtained in white micaceous laminæ. It melts at 198°, and solidifies a few degrees lower. It is more difficultly soluble in alcohol than amyrin. At 18°, 100 parts of alcohol dissolve 0·473 parts of acetyl-amyrin. Analysis gave 80·71 to 81·23 p.c. C., and 10·90 to 10·97 H., agreeing with the formula $C_{27}H_{44}O_2$, or $C_{25}H_{41}(C_2H_3O)O$, which requires 81 C., 11 H., and 8 O.

*Behaviour of Amyrin to Bromine.*—Bromine acts very strongly on solid amyrin, forming a blackish-green mass with strong evolution of hydrobromic acid.

A cold saturated alcoholic solution of amyrin was treated with an excess of bromine, a yellow precipitate being deposited after several hours, which was recrystallised from hot alcohol. The purified product forms a colourless indistinctly crystalline powder, which melts at 130°, with decomposition.

The analysis of this body gave 29·82 to 30·10 p.c. bromine, 59·58 to 59·67 carbon, and 7·95 to 8·17 hydrogen, numbers which may be represented approximately by either of the formulæ, $C_{40}H_{63}Br_3O$ and $C_{40}H_{65}Br_3O$, the former requiring 60·07 p.c. C., 7·89 H., 30·04 Br., and 2·00 O.; the latter, 59·93 C., 8·11 H, 29·96 Br., and 2·00 O. The formation of these compounds may be represented by the equations:—

$$8(C_{25}H_{42}O) + 30Br = 5(C_{40}H_{63}Br_3O) + 15HBr + 3H_2O.$$
$$8(C_{25}H_{42}O) + 20Br = 5(C_{40}H_{65}Br_3O) + 5HBr + 3H_2O.$$

*Products of the destructive Distillation of Amyrin.*—The yellow liquid

obtained from amyrin was subjected to fractional distillation, the temperature rising from 60° to 200° without giving products of constant boiling point. Combustion-analyses were made with several fractions taken off.

1. Fraction from 60°—70°.—Formed a colourless liquid, lighter than water, almost tasteless, and with pleasant smell, and giving by analysis 83·13, and (2) 83·47 p.c. carbon, and 14·50 to 14·75 hydrogen.

This portion of the distillate afterwards turned out to be a mixture of a body soluble in water, and another which was insoluble. The solution gave iodoform with iodine and potash. The undissolved portion was perfectly tasteless, while the soluble portion gave the water an aromatic taste and pleasant smell. The former dissolved iodine with a raspberry-red colour, while the original solution, before treatment with water, dissolved iodine with the colour of alcoholic tincture of iodine. The higher-boiling liquids were shaken up with potash, whereby a small quantity (more especially that distilling over between 201°—280°), was dissolved. After the alkaline solution had been acidified and distilled, a colourless watery liquid, with a few drops of a yellow oil, was obtained, smelling like creosote, and dissolving but slightly in water, readily in potash and alcohol. The filtered aqueous solution gave, with ferric chloride, at first a light blue colour, then turbidity with disappearance of colour. With chlorine and bromine-water, a white turbidity was formed. Sodium thiosulphate forms a flocculent precipitate. Mercurous nitrate after a short time, gave a black precipitate, and nitric acid produced a large quantity of oxalic acid. Combustions were also undertaken with two fractions left as residue after treatment with potash.

The fraction distilling at 185°—200° was a yellow thin liquid, sparingly soluble in water, with pleasant smell and aromatic taste, and giving by analysis 81·65 p.c. C., 11·47 H., and 6·58 O.

The fraction distilling at 260°—280° was a golden-yellow thick liquid, with slight smell and sharp taste, insoluble in water, and giving 84·40 C., 11·56 H., and 4·04 O.

Above 300°, a thick liquid with brown colour distilled over. The yellow powder observed at the end of the distilling operation consisted of three different bodies, which could not be separated and purified.

*Behaviour of Amyrin to Nitric Acid.*—Boiling nitric acid forms with amyrin a clear yellow solution, which, after evaporation, leaves a yellow mass. This mass gives an acid solution in water, as it contains oxalic acid. It reduces Fehling's solution when warmed. The greater part, however, is not soluble in water; it forms a resin acid, which, when boiled with alcohol, deposits after cooling a yellow powder. Dry hydrochloric gas does not act on amyrin alone, or dissolved in chloroform.

Analyses of a crystallisable "difficultly soluble" resin of elemi were made by Rose, Hess, Johnston, and others. They all found more than 84 per cent. of carbon, but Johnston's melting point of 149° shows that his preparation could not have been pure, unless it be assumed that his substance differed from that above described.

According to analysis, "brean" and "masopin" (Gmelin, vii, 1825—

1826), might be identical with amyrin, although their melting points are lower, viz., 157° and 155°. The comparison of amyrin with icacin, recently described by Stenhouse and Groves (*Lieb. Ann.*, **clxxx**, 253), as a body contained in the incense-tree, is worthy of notice, as Flückiger assumes it to be an elemi. It melts at 175°. Stenhouse and Groves give the formula $C_{46}H_{76}O$, but Flückiger thinks it probable that this body is similar to amyrin, and accordingly deduces from his analyses the formula $C_{45}H_{74}O = (C_5H_8)_9 + H_2O$. Icacin seems to replace amyrin in some kinds of elemi.

If we adopt Flückiger's formula, we obtain the following series of elemi-constituents:—

| | |
|---|---|
| Ethereal oil ..... | $(C_5H_8)_2$. |
| Icacin..... | $(C_5H_8)_9 + H_2O$. |
| Amyrin ..... | $(C_5H_8)_4 + H_2O$. |
| Bryoïdin..... | $(C_5H_8) + 3H_2O$. |

D. B.

## Cotoïn, the Crystalline Constituent of Coto Bark. By Julius Jobst (N. Repert. Pharm., xxv, 23—28).

Coto bark occurs in commerce in short pieces of from 10 to 20 mm. in length, some flat, others slightly curved, and possessing a very powerful aroma, recalling those of cloves, pepper, and cassia; the taste is aromatic. The bark is very brittle, and, owing to the quantity of resin it contains, difficult to reduce to fragments.

According to Wittstein, it contains (1) an essential oil, (2) a volatile alkaloïd similar to propylamine or trimethylamine, (3) a soft resin, (4) a hard resin.

The crystalline constituents which the author extracted amounted to 1·5 per cent. of the weight of the bark. They were obtained by extracting with ether, evaporating the liquid to one-tenth of its former volume, and mixing the residue with one-sixth of its bulk of petroleum ether. On addition of the latter, and removal of the ethylic ether by evaporation, resinous substances were deposited, and crystals were obtained from the supernatant liquid.

The cotoin thus obtained forms yellowish-white crystals which, under the microscope, appear as four-sided prisms; its melting point is 124°; alkalis dissolve it with a yellow colour, and it is reprecipitated on the addition of acids. Concentrated nitric acid dissolves it in the cold with a blood-red colour. Fehling's solution is reduced by it slowly in the cold, but with great rapidity on the application of heat.

The formula obtained was $C_{21}H_{20}O_6$. On precipitating with a lead salt, a precipitate was obtained having the composition $C_{21}H_{20}O_6 + 2PbH_2O_2$.

T. P. W.

# Analytical Chemistry.

**Estimation of Carbonic Acid in Waters (Irrigation and Sewage Waters, Springs and Rivers).** By A. HOUZEAU (Compt. rend., lxxxiii, 388—390).

THE method which the author proposes consists in disengaging successively the free and the combined carbonic acid, and absorbing it by 5 c.c. of a concentrated solution of soda of known strength, to which is added $\frac{1}{1600}$ of zinc oxide.

The apparatus consists of a flat-bottomed flask of 750 c.c. capacity, closed by a cork giving passage to two tubes, one of which is bent in the form of an S, and serves for the introduction of sulphuric acid, after the free carbonic acid has been expelled by prolonged ebullition. The other tube serves to conduct the carbonic acid into a flask of 210 c.c. capacity, in which is placed a part of the soda-solution, the other part being placed in a Will's tube connected with the flask. When all the carbonic acid has been expelled by a sufficiently prolonged ebullition (which usually takes place when about 170 c.c. of liquid have been condensed in the flask), the alkaline solution is poured out of the flask and tube into a foot-glass gauged to contain 200 c.c.; excess of chloride of barium is added; and the volume made up to 200 c.c. with the washings. After standing for a few minutes 50 c.c. of the clear solution are poured off from the precipitated carbonate of barium, and the soda estimated by standard acid. The difference between the amounts of soda before and after the experiment, gives the volume of acid corresponding with the carbonate of soda, and this volume multiplied by 2 gives the weight of the carbonic acid. The following are some results obtained with solutions of carbonates of known strength:—

| | I. | II. | III. | IV. |
|---|---|---|---|---|
| $CO_2$ taken.... | 25·0 mg. | 49·3 mg. | 80·0 mg. | 124·5 mg. |
| $CO_2$ found .. | 24·5 „ | 48·7 „ | 80·1 „ | 121·9 „ |

The method is, of course, applicable only to the estimation of carbonic acid in liquids which give off no other acid when heated with sulphuric acid.

H. W.

**New Process for the Detection and Estimation of Potash.** By AD. CARNOT (Compt. rend., lxxxiii, 390—393).

IN spite of the improvements introduced into the methods for the estimation of potash by Peligot and Schlœsing, the determination of this alkali has remained one of the most delicate operations of analytical chemistry. We have besides no very sinsitive reagent for the detection of potassium when it occurs in small quantity.

The author believes that he has solved these two difficulties by

means of the reaction given by salts of potassium with sodium thiosulphate and a salt of bismuth in a solution containing alcohol.

To prepare the solution, dissolve 1 part of subnitrate of bismuth in a few drops of hydrochloric acid, and about 2 parts of crystallised sodium thiosulphate in a few cubic centimeters of water; mix the two solutions together, and add a large excess of absolute alcohol.

With a solution containing potassium a yellow precipitate is immediately formed; with an insoluble salt a characteristic yellow coloration is produced.

All the salts of potash, both mineral and organic, lend themselves equally well to this reaction. Other metals do not interfere, except barium and strontium, which produce white precipitates of the double thiosulphates. The double thiosulphate of bismuth and potassium is too unstable to allow the quantity of potassium to be calculated directly from its weight. The precipitate, after being washed with alcohol, is therefore dissolved in water, and the bismuth precipitated as sulphide with ammonium sulphide; this precipitate is washed by decantation, dried at 100°, and weighed. The weight of potassium is then found by multiplying the weight of bismuth sulphide by the fraction $\frac{3K_2O}{Bi_2S_3} = 0{\cdot}549$.

H. W.

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**On the different Rotatory Powers Exhibited by Cane-sugar according to the Process Employed to Measure it.** By L. CALDERON (Compt. rend., lxxxiii, 393).

THE deviations which an optically active substance produces on the mean yellow ray and on the extraordinary image at the minimum of brightness measured with the transition-tint, are known to be unequal. Till lately the rotatory powers of active substances were measured by the transition-tint, but the monochromatic yellow flame has now come into use. It was with this that Jellet and Cornu obtained the number $\alpha_D = 67° 18'$ as the rotatory power of cane-sugar.

The following table gives the results obtained in eighteen series of six experiments, making use of tubes 0·2 to 0·3 mm. long:—

| Sugar in 1 litre. | Length of tube m. | Mean deviation by experiment. | Rotatory power. | Mean. | Old determinations. |
|---|---|---|---|---|---|
| 99·855 | 0·3 | 21° 56′ | 73° 12′ | 73° 12′ | 73° 48′ (by Berthelot) |
| 199·710 | 0·3 | 43° 52′ | 73° 13′ | | |
| 199·710 | 0·2 | 29° 14′ | 73° 11′ | | |
| 99·855 | 0·3 | 20° 8′ | 67° 12′ | 67° 9′ | 67° 18′ (by A. Girard) |
| 199·710 | 0·3 | 40° 12′ | 67° 5′ | | |
| 199·710 | 0·2 | 26° 50′ | 67° 10′ | | |

Mean rotatory power (transition tint) ..... $a_j = 73° 12'$
Mean rotatory power (monochromatic flame) . $a_D = 67° 9'$

6° 3′

It must be remembered that these two deviations vary according to the law of dispersion proper to each active substance.

H. W.

**Process for Estimating Hydrocarbons, and particularly Marsh-gas, in Mines.** By J. COQUILLON (Compt. rend., lxxxiii, 394).

THIS paper treats of the use of a palladium-wire, heated to redness by an electric current, in analysing mixtures of marsh-gas and air. The author states that palladium, unlike platinum, causes the combustion of the marsh-gas without an explosion.

H. W.

**On the Fraudulent Coloration of Wines.** By ARM. GAUTIER (Bull. Soc. Chim. [2], xxv, 483—498; 530—538).

THE following table (A) has been prepared in order to show the action of reagents upon the substances employed for fraudulent coloration of wines, both when the substances in question are in the pure state, and when they are mixed with genuine wines in such proportion that, of the total intensity of the colour of the mixture, about one-fifth was due to the foreign colouring substance. In all cases, before commencing the tests, the samples were shaken for some minutes with one-tenth their volume of egg-albumin (which had been previously diluted with 1½ times its bulk of water) and then filtered, whereby the filtrate was rendered comparatively richer in the adulterating substances.

TABLE A.—*Action of Reagents on the Colouring Matters used to adulterate Wines, and on Mixtures of those Matters with Red Wines, to the extent of 20 per cent. of the Intensity of the Colour of the Liquid examined.*

| Nature of the liquid examined. | A. To 1 c.c. of the unclarified wine add 3 to 5 c.c. of 1-200th sodium carbonate, according to the intensity of the colour and the acidity. | B. Heat the preceding to boiling |
|---|---|---|
| Pure wine ..... | Coloration bluish-green, grey, slightly greenish, according to the wine. With *aramon*, lilac. | The liquid becomes yellow; has a tendency to discolour. The trace of lilac, had there been any, disappears. |
| Pure Brazil wood .... | Red currant ..... | " |
| Brazil wood, 1 part / Wine ..... 4 parts | Brown-lilac, or brown tinged with maroon. | Wine colour ..... |

| Nature of the liquid examined. | C. To 2 c.c. of clarified wine add 1·5 to 2 c.c. of an 8 per cent. solution of sodium bicarbonate charged with carbonic acid; examine the colour after 2 minutes. | D. To 2 c.c. of clarified wine add 3 c.c. of dilute ammonia (1 c.c. of ammonia to 10 of water); then dilute with 5 c.c. of water. |
|---|---|---|
| Pure wine ..... | Deep grey with a little green, or sometimes violet. | Greenish-grey blue or greenish grey, very faintly lilac. |
| Pure Brazil wood .... | Red currant ..... | Red currant. |
| Brazil wood, 1 part } Wine ..... 4 parts } | Wine-lilac ..... | Lilac, soiled with grey or maroon. |

| Nature of the liquid examined. | E. 2 c.c. of clarified wine are treated with 2 c.c. of saturated baryta water, and filtered after 15 minutes. Colour of the filtrate. | F. The filtrate E is acidulated with acetic acid. |
|---|---|---|
| Pure wine ..... | Dirty yellow, with a little green. | Liquid faintly roseate, in certain rare cases nearly colourless. |
| Pure Brazil wood .... | " | " |
| Brazil wood, 1 part } Wine ..... 4 parts } | Red-brown ..... | Onion-skin, or nearly colourless yellow. |

| Nature of the liquid examined. | G. To 2 c.c. of clarified wine add 3 to 4 c.c. of saturated solution of borax, depending upon the intensity of the colour of the wine. | H. To 4 c.c. of clarified wine add 1 c.c. of a 10 per cent. solution of alum, and 1 cc. of a 10 per cent. solution of sodium carbonate. Colour of the lake. |
|---|---|---|
| Pure wine ..... | Liquid grey-blue or greenish; flax blossom; sometimes a trace or more of lilac. Liquid bluish- or greenish-grey. | Lake bluish-green or greenish. |
| Pure Brazil wood .... | Red currant ..... | " |
| Brazil wood, 1 part } Wine ..... 4 parts } | Wine-lilac ..... | Lilac-lake, running into brick-red. |

| Nature of the liquid examined. | K. Colour of the filtrate from H. | L. To 2 c.c. of clarified wine add 1 c.c. of subacetate of lead of 15° B. Shake. Filter. Colour of precipitate. |
|---|---|---|
| Pure wine ..... | Clear bottle-green. Almost colourless with certain rare varieties. | Ashy blue-green, rarely apple-green or yellowish-green. |
| Pure Brazil wood .... | " | Brown-lilac. |
| Brazil wood, 1 part<br>Wine ..... 4 parts | Liquid, grey, with a little maroon. | Precipitate ashey-blue, tinged with yellow, or brick-red. |

| Nature of the liquid examined. | M. Colour of filtrate from L. | N. To 1 c.c. of clarified wine add 1 c.c. of acetate of alumina of 2° B. Colour of the liquid. |
|---|---|---|
| Pure wine ..... | Decolorised ..... | Liquid wine-lilac. *Aramon* is nearly decolorised. |
| Pure Brazil wood .... | If an excess of lead salt is added, and the fluid heated, red currant. | Preserves its original colour. |
| Brazil wood, 1 part<br>Wine ..... 4 parts | Decolorised, or very slightly reddish. | Old wine red, or roseate. |

| Nature of the liquid examined. | O. To 1 c.c. of clarified wine add 4 drops of aluminate of potash (obtained by adding alum to a solution of alumina in potash). Filter the mixture. | P. To 0·1 gram of barium peroxide add 5 drops of a 5 per cent. solution of tartaric acid, and then 3 c.c. of clarified wine. Examine the colour 18 hours afterwards. |
|---|---|---|
| Pure wine ..... | Lilac, faintly rose; tendency to decolorise. | Liquid scarcely rose-tinted; a trace (or none) of orange in contact with the peroxide. |
| Pure Brazil wood .... | " | " |
| Brazil wood, 1 part<br>Wine ..... 4 parts | Onion-skin, or slightly rose.. | Liquid yellow, without rose colour even in 10 hours. Large orange deposit in contact with the peroxide. |

| Nature of the liquid examined. | A. | B. |
|---|---|---|
| Pure logwood..... | Red-purple or violet ..... | " |
| Logwood .. 1 part<br>Wine..... 4 parts | Same colorations as pure wine. | Lilac, or wine-violet. |
| Pure cochineal ..... | Lilac ..... | " |
| Cochineal .. 1 part<br>Wine ..... 4 parts | Grey flax-blossom, or grey with tinge of lilac. | The grey tinged with lilac is unchanged. |
| Pure fuchsine..... | Rose ..... | " |
| Fuchsine .. 1 part<br>Wine..... 4 parts | Colour greenish-grey, sometimes with lilac tint. | The rose-violet or rose-lilac tints disappear. |
| Portugal berries, pure | Violet-rose..... | " |
| Phytolacca.. 1 part<br>Wine ..... 4 parts | Dark violet, or lilac ..... | Yellow-grey with little maroon, which increases with the amount of phytolacca. |

| Nature of the liquid examined. | C. | D. |
|---|---|---|
| Pure logwood..... | Rose wine-colour ..... | Violet-lilac. The violet tends to disappear with an excess of reagent, and to reappear on heating. |
| Logwood .. 1 part<br>Wine..... 4 parts | Deep greenish-grey ..... | Greenish-grey. |
| Pure cochineal ..... | Lilac ..... | Violet-lilac. |
| Cochineal .. 1 part<br>Wine..... 4 parts | Grey, tinted with lilac or violet. | Greenish-grey, or greenish grey-brown. |
| Pure fuchsine..... | Rose ..... | Rose. Decolorised by an excess of reagent. |
| Fuchsine .. 1 part<br>Wine..... 4 parts | Wine lees roseate..... | Greenish-grey, with or without tinge of rose. |
| Portugal berries, pure | Violet-rose..... | Violet-rose. |
| Phytolacca.. 1 part<br>Wine ..... 4 parts | True lilac ..... | Deep grey with a little maroon or lilac. |

| Nature of the liquid examined. | E. | F. |
|---|---|---|
| Pure logwood..... | " | " |
| Logwood .. 1 part<br>Wine..... 4 parts | Dirty greenish-yellow ..... | Scarcely roseate. |
| Pure cochineal ..... | " | " |
| Cochineal .. 1 part<br>Wine..... 4 parts | Dirty greenish-yellow ..... | Very distinctly rose. |
| Pure fuchsine..... | " | " |
| Fuchsine .. 1 part<br>Wine ..... 4 parts | Dirty greenish-yellow ..... | Distinctly rose. |
| Portugal berries, pure | " | " |
| Phytolacca.. 1 part<br>Wine ..... 4 parts | Dirty greenish-yellow ..... | Distinctly rose. |

| Nature of the liquid examined. | G. | H. |
|---|---|---|
| Pure logwood..... | Rose wine-colour ..... | Lake violet-blue. |
| Logwood .. 1 part<br>Wine..... 4 parts | Grey-blue (flax blossom) slightly tinged with maroon | Lake bluish-green tinged with violet, becoming more violet by drying in the air. |
| Pure cochineal ..... | Lilac ..... | Lake rose. |
| Cochineal .. 1 part<br>Wine..... 4 parts | Lilac or bluish-grey tinged with lilac. | Lake bluish, slightly roseate. |
| Pure fuchsine.. ..... | Rose ..... | " |
| Fuchsine .. 1 part<br>Wine..... 4 parts | Bluish-grey with lilac; sometimes the latter is very faint. | Lake bluish or greenish, slightly roseate. |
| Portugal berries, pure | Violet-rose..... | Lake violet. |
| Phytolacca.. 1 part<br>Wine ..... 4 parts | Lilac, or grey-blue with little lilac. | Bluish-green, or greenish, slightly roseate with more phytolacca. |

| Nature of the liquid examined. | K. | L. |
|---|---|---|
| Pure logwood..... | " | Somewhat violet. |
| Logwood .. 1 part<br>Wine..... 4 parts | Clear bottle-green..... | Blue. Rather more violet than with wine only. |
| Pure cochineal ..... | Liquid always rose, more or less deep. | Deep violet-lilac |
| Cochineal .. 1 part<br>Wine..... 4 parts | Rose-lilac ..... | Ashy-blue, clear green. |
| Pure fuchsine..... | " | No precipitate. |
| Fuchsine .. 1 part<br>Wine..... 1 parts | Clear green ..... | Ashy blue, sometimes slightly rose tinted. |
| Portugal berries, pure | " | Violet-maroon, slight; soluble in excess. |
| Phytolacca.. 1 part<br>Wine ..... 4 parts | Lilac ..... | Ashy greenish-blue. |

| Nature of the liquid examined. | M. | N. |
|---|---|---|
| Pure logwood..... | Colourless, or but slightly lilac. | Becomes violet-blue. |
| Logwood .. 1 part<br>Wine..... 4 parts | Decolorised, or but very slightly yellow. | Violet or lilac. |
| Pure cochineal ..... | Lilac, almost colourless .... | Rose-lilac. |
| Cochineal .. 1 part<br>Wine..... 4 parts | Decolorised ..... | Wine-lilac. |
| Pure fuchsine..... | Rose ..... | Rose. |
| Fuchsine .. 1 part<br>Wine..... 4 parts | Rose ..... | Lilac or rose. |
| Portugal berries, pure | Decolorised if the lead salt is not in excess, otherwise yellow-red. | Violet-rose. |
| Phytolacca.. 1 part<br>Wine ..... 4 parts | Decolorised, or very faintly roseate. | Wine-lilac, or distinctly lilac. |

| Nature of the liquid examined. | O. | P. |
|---|---|---|
| Pure logwood..... | Precipitate blue or somewhat violet. | " |
| Logwood .. 1 part<br>Wine..... 4 parts | Rose tinged with violet .... | Like the preceding mixture. |
| Pure cochineal ..... | Rose-lilac ..... | " |
| Cochineal .. 1 part<br>Wine..... 4 parts | Rose ..... | Liquid rose, with tinge of orange-yellow in contact with the peroxide. |
| Pure fuchsine..... | Rose ..... | " |
| Fuchsine .. 1 part<br>Wine..... 4 parts | Rose ..... | Liquid scarcely rose tinted. Orange deposit in contact with the peroxide. |
| Portugal berries, pure | " | " |
| Phytolacca.. 1 part<br>Wine ..... 4 parts | Bright rose ..... | Liquid distinctly rose. Orange deposit in contact with the peroxide. |

| Nature of the liquid examined. | A. | B. |
|---|---|---|
| Hollyhock, pure..... | Dark bottle-green..... | " |
| Hollyhock.. 1 part<br>Wine ..... 4 parts | Greenish, slightly blue, or greenish-grey. | Partially decolorised, slightly greenish-grey. |
| Beetroot, pure ..... | Rose, or yellowish-red, which is persistent. | " |
| Beetroot ... 1 part<br>Wine ..... 4 parts | Yellowish-grey if the beet-juice was fermented; faint yellowish-red if fresh. | Tends to be decolorised if the beet-juice was old; yellowish-grey, touched with red, if fresh. |
| Black elder, pure..... | Violet-lilac, changing to dark bluish-grey, then to bluish-green. | " |
| Black elder.. 1 part<br>Wine ..... 4 parts | Dark green with lilac tinge. | Dark greenish-grey. |

| Nature of the liquid examined. | C. | D. |
|---|---|---|
| Hollyhock, pure..... | Dark greenish-grey ..... | Bottle-green. |
| Hollyhock .. 1 part<br>Wine ..... 4 parts | Grey with little green or blue | Bottle-green darkened with grey. |
| Beetroot, pure ..... | Rose, or yellowish-red, which is persistent. | Yellow if the beet-juice was fermented, roseate if new. |
| Beetroot.... 1 part<br>Wine ..... 4 parts | Reddish-yellow or lilac-brown | Dirty yellowish-grey with a little maroon if the beet-juice was fresh and not fermented. |
| Black elder, pure ..... | Wine lilac ..... | Fine green. |
| Black elder.. 1 part<br>Wine ..... 4 parts | Remains lilac for an instant, then rapidly changes to grey with greenish-blue. | Dirty greenish-grey. |

| Nature of the liquid examined. | E. | F. | G. |
|---|---|---|---|
| Hollyhock, pure..... | ,, | ,, | Dark infusion of tea, coloured. |
| Hollyhock .. 1 part<br>Wine ..... 4 parts | Dirty greenish-yellow. | Scarcely roseate | Greenish blue-grey. |
| Beetroot, pure ..... | ,, | ,, | Rose, or yellowish-red, according to the age of the infusion. |
| Beetroot.... 1 part<br>Wine ..... 4 parts | Clear yellowish | Yellowish, or colour of onion skin, slightly rose. | Grey ; a little brown-violet if the beet-juice was recent. |
| Black elder, pure..... | ,, | ,, | Wine colour. |
| Black elder.. 1 part<br>Wine ..... 4 parts | Dirty greenish-yellow. | Liquid is roseate. | Lilac, or greenish grey-blue, scarcely lilac. |

| Nature of the liquid examined. | A. | B. |
|---|---|---|
| Dwarf elder, pure .... | Bottle-green darkened with grey. | " |
| Dwarf elder, 1 part<br>Wine ..... 4 parts | Green with lilac tinge, or grey slightly green. | The green tends to disappear on heating. |
| Privet, pure ..... | Dark green..... | " |
| Privet..... 1 part<br>Wine ..... 4 parts | Dark green to greenish-grey | Changes to dirty yellowish. |
| Whortleberries, pure.. | Wine colour; more reagent changes it to grey-lilac and grey tinged with lilac. | Becomes yellowish-grey. |
| Whortleberries, 1 pt.<br>Wine ..... 4 parts | Yellowish-grey with a little lilac or rose. | Becomes deep grey. |
| Indigo, pure ..... | Blue..... | " |
| Indigo ..... 1 part<br>Wine (not clarified), 4 parts | Greenish, slightly blue ..... | Tends to become yellow. |

| Nature of the liquid examined. | C. | D. |
|---|---|---|
| Dwarf elder, pure .... | Wine-red..... | Dark bottle-green. |
| Dwarf elder, 1 part<br>Wine ..... 4 parts | Lilac, with grey or grey tinged with maroon. | Dark green with grey, possibly tinged with maroon. |
| Privet, pure ..... | Dark grey tinged with maroon. | Dark green. |
| Privet..... 1 part<br>Wine ..... 4 parts | Greenish-grey. | Bluish, greenish-blue, or greenish-grey, according to the variety of wine. |
| Whortleberries, pure.. | Remains lilac; an excess of reagent rapidly changes it to grey slightly red. | Maroon by transmitted, grey bottle-green by reflected light. |
| Whortleberries, 1 pt.<br>Wine ..... 4 parts | Yellowish-grey, frequently with a little red. | Greenish-grey or yellowish-grey. |
| Indigo, pure..... | Liquid blue, tending to become green. | Blue, slowly decolorised. |
| Indigo ..... 1 part<br>Wine (not clarified), 4 parts | Bluish, or greenish-blue. | Oak-leaf green. |

| Nature of the liquid examined. | E. | F. | G. |
|---|---|---|---|
| Dwarf elder, pure .... | " | " | Colour of port wine. |
| Dwarf elder, 1 part<br>Wine ..... 4 parts | Clear greenish-yellow. | Scarcely roseate. | Lilac. |
| Privet, pure ..... | " | " | Dirty reddish-rose. |
| Privet..... 1 part<br>Wine ..... 4 parts | Yellowish with a little green. | Scarcely roseate. | Greenish grey-blue tinged with lilac. |
| Whortleberries, pure.. | " | " | Dirty yellow tinged with lilac. |
| Whortleberries, 1 pt.<br>Wine ..... 4 parts | Greenish-yellow | Faintly roseate. | Grey with a little lilac. |
| Indigo, pure ..... | Becomes green, then slowly decolorised. | " | Blue. |
| Indigo ..... 1 part<br>Wine (not clarified), 4 parts | Dirty green-grey. | Roseate ..... | Bluish-green. |

*Notes to Table A.*

1. Each wine reacts in a slightly different manner, according to its age, variety, &c. This table refers to wines of five to fifteen months old, and particularly to the following:—Pinot, Carignane, Teinturier, Carbenet. Aramon gives special reactions not shown here.

2. The word *pure* means *not mixed with wine*. The reactions shown were obtained by acting upon solutions of the substances in water containing 10 per cent. of alcohol, and made of such strength that the colours corresponded in intensity with those of the wines being examined.

3. *Brazil wood* 1 *part, wine* 4 *parts* means that the intensity of the colour of the liquid examined resulted from the mixture of the decoction of Brazil wood and of wine in the proportions named. These proportions refer only to the intensity of the coloration, and represent but a very minute ponderable quantity of the adulterating substance.

In order to make these reactions practically useful, much care has been given to the relative constancy and value of each of them, and as a result a systematic method of research has been arranged, and is shown in table B.

Even with every precaution, in the process of examination, cases may arise in which an amount of uncertainty may exist. In such cases further examination by other reactions must follow; the specimen is submitted several times to a series of new tests by which the adulteration may be detected. The mention of one and the same substance may for that reason occur in various places in table B.

*Preliminary Preparation of the Sample.*—The wine to be examined is mixed with one-tenth its volume of white of egg previously diluted with 1½ parts of water; well shaken, and, after standing for half-an-hour, filtered. (If the wine was very poor in tannates, a few drops of a fresh aqueous solution of tannin should be added previous to the

agitation with albumin.) The filtrate is treated with dilute bicarbonate of soda, until its reaction is but *very* feebly acid. All the reactions of table B must be made on this liquid (except those for indigo, which are executed upon the albuminous precipitate).

TABLE B.—*Systematic process to be followed for the Detection of the nature of the Foreign Colouring Matters added to Wines.*

| | |
|---|---|
| A. The filtrate from the albuminous precipitate having been set aside, the precipitate is washed until the washings are almost colourless.<br>Two cases may present themselves. | (*a.*) The precipitate after washing remains wine-coloured, lilac or maroon: *natural wine;* or *may be adulterated with the greater part of the substances usually employed.* Pass to C.<br>(*b.*) The precipitate is of a very deep wine-colour, violet-blue, or bluish: *wines from the deepest-coloured grapes:* or, *wines coloured with indigo.* Pass to B. |
| B. The precipitate *b* from A is washed with water, then with alcohol of 25 per cent. A part is then removed and boiled with alcohol of 85 per cent., and filtered. | (*a.*) The filtrate is *rose*, or *wine-coloured.* A portion of the precipitate is removed from the filter, suspended in water, and carefully saturated with dilute carbonate of potash. The colour changes to dirty-brown or to blackish-brown: *natural wine;* or *may be adulterated with substances other than indigo.* Pass to C.<br>(*b.*) The filtrate is *blue.*<br>A portion of the precipitate suspended in water and treated with dilute carbonate of potash, as above directed, affords a deep-blue liquid: which is changed to yellow by an excess of the reagent. Various preparations of indigo. *Indigo.* |
| C. 2 c.c. of wine are treated with 6 to 8 c.c. of a $\frac{1}{200}$th solution of carbonate of soda, which must be added in slight excess (1 c.c.) after the change of colour. | (*a.*) The liquid becomes *lilac* or *violet;* sometimes the tint becomes only winey, or dashed with violet. *Brazil wood, cochineal, Portugal berries, fuchsine, wines of certain sorts; fresh beetroot, logwood, whortleberries,* both *elders, Portugal berries.* Pass to D.<br>(*b.*) The liquid becomes *bluish-green,* sometimes with a faint lilac tint; *wine, hollyhock, privet berries, whortleberries, logwood,* both *elders, Portugal berries, fuchsine.* Pass to M.<br>(*c.*) The liquid becomes *greenish-yellow,* without any blue or violet. *Beetroot,* in either old or fermented decoction: *whortleberries.* Certain rare varieties of wines. Pass to L. |

| | |
|---|---|
| D. The liquid C (*a*) is heated to boiling. | (*a.*) The liquid remains wine-violet, rose, or wine-lilac, or becomes a brighter lilac. *Brazil wood, logwood, cochineal certain varieties of wines.* Pass to E.<br>(*b.*) The colour disappears, or is replaced by a yellow, or maroon, or reddish tint. *Wine, fuchsine,* both *elders, whortleberries, Portugal berries,* fresh *beetroot.* Pass to F. |
| E. Treat 4 c.c. of the wine with 2 c.c. of each of a 10 per cent. solution of alum, and a 10 per cent. solution of crystallised carbonate of soda. Filter. | (*a.*) Clear, yellowish-green lake (which may be bluish from mixtures of wines containing aramon). Filtrate colourless, becoming very slightly yellow on warming; its own volume of acetate of alumina at 2° B. almost wholly decolorises it. On acidification with acetic acid after treatment with its own volume of a saturated solution of barium hydrate, the wine becomes clear greenish-yellow.—*Aramon pure or mixed.*<br>(*b.*) Greenish-blue lake, or dirty, yellowish-green, according to the varieties present; sometimes very slightly winey. Filtrate bright rose; gradually discoloured on warming, though retaining a tinge of lilac, not discoloured by lime-water in the cold.—*Cochineal.*<br>(*c.*) Winey-violet lake, which darkens on exposure to air. Filtrate *bottle-green,* or grey, faintly red (if much logwood is present). The filtrate becomes green on warming.—*Logwood.*<br>(*d.*) Lilac, or maroon-lilac lake. Filtrate greyish, with tint of maroon. On boiling, this liquid becomes fine old wine coloured.—*Brazil wood.* |
| F. Treat 4 c.c. of the wine with alum and sodium carbonate (as explained in E); add to the mixture two or three drops of very dilute sodium carbonate, and filter. | (*a.*) The filtrate is lilac or winey; *Portugal berries; fresh beetroot.* Pass to G.<br>(*b.*) The filtrate is bottle-green, or reddish-green; *wine, fuchsine, black elder, whortleberries, beetroot.* Pass to H. |
| G. Treat 2 c.c. of the wine with sub-acetate of lead of 15° B. Shake. Filter. | (*a.*) The filtrate is rose, which persists, even when made slightly alkaline; it disappears slowly on boiling. Lime-water destroys the rose colour.—*Portugal berries.*<br>(*b.*) The filtrate is yellowish or brownish-red.—*Fresh beetroot.* |

| | |
|---|---|
| H. The alum-lake obtained from F (*b*) was:— | (*a.*) *Deep blue.* On treating the clarified wine with a few drops of acetate of alumina, it becomes a decided violet, or wine-violet. Both *elders.* Pass to I.<br>(*b.*) Bluish-green, green, or faintly rose-tinted. *Wine, whortleberries, beetroot, fuchsine.* Pass to J. |
| I. After the test H (*a*) treat a fresh quantity of 2 c.c. (according to its acidity, and the deepness of its tint) with 1·5 to 2 c.c. of an 8 per cent. solution of bicarbonate of soda charged with carbonic acid. | (*a.*) The liquid remains lilac for a moment, then rapidly changes to a greenish grey-blue. Another specimen, treated with carbonate of soda (according to C) and heated to boiling, becomes dark greenish-grey.—*Black elder.*<br>(*b.*) The liquid retains a lilac tint; or grey with mixture of maroon, or dirty lilac. Another specimen, treated with carbonate of soda (according to C), has a tendency to discolour on heating, the green being replaced by red.—*Dwarf elder.* |
| J. Treat 5 c.c. of the clarified wine with a slight excess of ammonia; heat to boiling, and after cooling, shake with 10 c.c. of ether. Decant, and evaporate the ether, and treat the residue left on evaporation with acetic acid. | (*a.*) The liquid becomes red.—*Fuchsine.*<br>(*b.*) The liquid does not become red. *Wine, whortleberries, fresh beetroot.* Pass to K. |
| K. Another specimen is treated according to C, with carbonate of soda. | (*a.*) The colour darkens, or becomes red on heating. *Whortleberries, fresh beetroot.* Pass to L.<br>(*b.*) The greenish or bluish-green liquid, possibly having a winey tinge; has a tendency to discolour on heating.—*Natural wine.* |
| | (*a.*) Liquid is deep grey, faintly greenish, green, sometimes green with very slight lilac tint. The clarified wine treated with an equal volume of saturated baryta-water, filters, after standing for 15 minutes, dirty-yellow, or slightly greenish. With an equal bulk of acetate of alumina of 2° B., it gives a lilac wine-coloured filtrate. With a few drops of aluminate of potash, no change of colour. With carbonate of soda used according to C, the liquid tends to lose its colour on heating. With peroxide of barium, used according to Table A, column P, the liquid |

is faintly rose-tinted, with or without an orange-coloured deposit on the barium peroxide.—*Natural wine.*

With the general characters above indicated, if with the baryta-water it affords a Madeira-coloured filtrate, changing to buff on acidulation with acetic acid; if with borax it becomes deep green, with caste of blue; if with alum, and sodium carbonate (used as shown at E), a deep bottle-green, with trace of blue, precipitate falls; and if with acetate of alumina, it remains rose-coloured, and does not change to violet blue.—*Teinturier.*

L. Treated with bicarbonate of soda, according to rules shown at I.

(*b.*) By the treatment L, the liquid becomes reddish-yellow, or brown-lilac. Treatment with acetate of alumina yields a clear lilac filtrate. With a few drops of aluminate of potash, the colour becomes that of the skin of an onion, and with a larger quantity of the reagent the colour is green, tinged with maroon. With sodium carbonate, employed as at C, the fluid passes to yellowish, or greyish-yellow with tinge of red. With barium peroxide, flesh-coloured liquid with considerable orange-coloured deposit in contact with the peroxide.—*Beetroot*, fermented or not.

(*c.*) By the same treatment (L) the liquid is yellowish-grey, with tinge of green or red. With baryta-water (according to L) the filtrate is yellowish olive-green. With acetate of alumina (according to L) filtrate is bluish-violet or violet-lilac. With aluminate of potash (L) bright rose, becoming yellowish-green with an excess of reagent. With carbonate of soda (according to C) the liquid becomes deep grey on heating. With barium peroxide (according to Table A) the fluid is bleached, or remains very slightly roseate, with a trace of orange deposit in contact with the peroxide.—*Whortleberries.*

M. The mixture of wine and alkaline carbonate (C) *b* is heated to boiling.

(*a.*) The mixture becomes violet, or lilac-violet.—*Logwood.*

(*b.*) The mixture tends to become discoloured, or changes to yellowish-green, or dark green, or maroon-green: *natural wines*, *whortleberries*, both *elders*, *privet*, *Portugal berries*, *fuchsine.* Pass to N.

N. Treat the wine

(*a.*) The colour of the filtrate is lilac. *Portugal berries.*

| | |
|---|---|
| with alum and sodium carbonate, as directed at E, and filter. | (*b.*) The filtrate changes to bottle-green, or reddish-green: *natural wines; whortleberries, hollyhock, privet,* both *elders, fuchsine.* Pass to O. |
| O. Treat 2 c.c. of the clarified wine with 3 or 4 c.c. of a saturated solution of borax (according to the intensity of the colour of the wine.) | (*a.*) The liquid remains wine-lilac or with some violet tinge. Both *elders, whortleberries, privet.* Pass to P.<br>(*b.*) The fluid becomes bluish-grey; grey flax-blossom; greenish-, or bluish-grey, with very faint trace of lilac. *Pure wine, whortleberries, hollyhock, fuchsine.* Pass to R. |
| P. Treat a new portion of wine with sodium bicarbonate (as explained at I). | (*a.*) The tint, at first lilac, changes afterwards to grey, slightly brownish, or to maroon. If a new portion be treated with carbonate of soda (according to C) and then heated to boiling, it becomes clear, and loses its green tint. The lake, obtained (according to E) is deep blue-green.—*Dwarf elder.*<br>(*b.*) The specimen remains grey tinged with green, bottle-green or yellowish. Sometimes (black elder) after the action of the reagent it acquires a lilac tint, which almost immediately disappears, changing to a greenish grey-blue. *Whortleberries, black elder, privet.* Pass to Q. |
| Q. Treat a specimen of the wine with alum and sodium carbonate (as directed at E). Shake the mixture, and after a few moments throw it on a filter. | (*a.*) The lake remaining on the filter is deep green-blue: the filtrate is clear bottle-green. A sample treated with sodium carbonate according to C darkens and becomes grey, and slightly greenish on heating to boiling.—*Black elder.*<br>(*b.*) The lake is clear bluish, or greenish. The filtrate is clear bottle-green. A sample treated with sodium carbonate (as directed at C) and heated to boiling changes to dirty yellowish.—*Privet.*<br>(*c.*) The lake is ash-green, faintly rose-tinted. The filtrate is bottle-green with tint of maroon. A sample treated with sodium carbonate according to C becomes deep-grey on being heated to boiling.—*Whortleberries.* |
| R. Treat a specimen of the wine with ammonia and ether (as directed at J). | (*a.*) The ether being decanted and evaporated, the remaining liquid, on treatment with acetic acid, becomes rose coloured.—*Fuchsine.*<br>(*b.*) The liquid left after the evaporation of the ether, on acidification with acetic acid, does not become rose-coloured. *Natural wines, hollyhock, whortleberries.* Pass to S. |

| | |
|---|---|
| S. A sample is treated with its own bulk of a solution of acetate of alumina at 2° B. | (*a.*) The colour of the mixture remains winey: *Natural wines, whortleberries.* Differentiate between them as directed at L *a* and L *c.*<br>(*b.*) The colour of the mixture becomes violet-blue: *Hollyhock, whortleberries.* Pass to T. |
| T. A specimen is treated with alum and sodium carbonate (as directed at E). After some minutes it is filtered. | (*a.*) The lake is clear green, slightly bluish, and rose-tinted; filtrate is bottle-green, with dash of maroon. With borax (as at O) particularly if the sample has been concentrated, the liquid is grey with trace of lilac. Two c.c. of the liquid treated with 3 c.c. of dilute ammonia (1 vol. liquid ammonia with 10 vols. of water), and the mixture diluted with its own bulk of water gives a tint which is yellowish-grey, greenish, or clear greenish-grey. The other characteristics as at L.—*Whortleberries.*<br>(*b.*) The lake is green, slightly bluish, quite free from rose, filtrate clear bottle-green. With borax, the liquid is greenish-blue grey. With ammonia (as above), dark bottle-green. With aluminium acetate (as at S) bluish-violet coloration.—*Hollyhock.* |

Although somewhat difficult, this systematic method serves for the discovery of several colouring matters mixed in one wine, if the indications of the Tables A and B are carefully observed and followed. It is always desirable to determine the presence of fuchsine by the special reactions given further on. By means of Table B the presence of one or several of the colouring matters may be shown, or at least their existence rendered very probable, but before finally deciding, it is as well to verify by repeating for the substances so found the reactions of Table A on the sample; and also the more special characteristic reactions given further on for the identification of those substances.

*Special Reactions for the Detection of certain of the Colouring Matters mixed with Wines. Brazil Wood.*—Even a very strong clarification (2 or 3 times more albumin than mentioned at the head of Table B) does not wholly decolorise the adulterated wine. It becomes yellow-buff, which on exposure to the air gradually changes to red.

If a wine that has been adulterated with Brazil wood is clarified, and then a skein of scoured silk, washed with dilute tartaric acid, is soaked in it for 24 hours and then withdrawn, washed, and dried at 60°—70°, the silk will be found to be dyed lilac-maroon, or red. The skein remains wine-coloured or lilac in pure wine.

If the dyed silk be now dipped into dilute ammonia, and then heated to 100° for a moment, it becomes lilac-red, if the wine was adulterated with Brazil wood; while if the wine was pure, the change

would be to deep grey with scarcely a tinge of its original colour. If the ammonia be replaced by lime-water, the skein changes to ash-grey if Brazil wood was present, but to a dark dirty yellowish-red if the wine were pure. Finally, if the dyed skein be dipped in aluminium acetate and then heated to 100°, it retains its wine-red lilac colour. This reaction differentiates Brazil wood from logwood.

*Logwood.*—If the colour due to logwood is in excess in the wine, ammonia gives it a shade of violet; if the proportion of logwood is small, the reactions (B) (L) (N) of Table A, which are very delicate, should be tried.

Treated with a skein of silk prepared in the manner described for Brazil wood, it becomes dyed lilac-red or maroon, changed by dilute ammonia to violet-blue tinged with grey, and by acetate of aluminium to bluish-violet.

*Cochineal.*—The lilac or roseate tints due to the reactions (A) (B) (H) (K) of Table A are very sensitive, the last being very characteristic; the only substance likely to be confounded with it being the (Phytolacca) *Portugal berries*, which is differentiated by the reaction (B) of the same Table.

A skein of scoured silk mordanted with aluminium acetate, soaked in the clarified wine for 20 hours, is dyed of a wine-violet colour analogous to that of a pure wine, on being dried at 100°.

The colour does not change even at 100° by cupric acetate (exclusion of fuchsine), but if the skein be dipped into a dilute solution of zinc chloride, heated to 100°, and then wetted with sodium carbonate, washed with water and dried, the colour becomes fine purple; whereas, with pure wine, the tint would remain sombre grey-lilac.

Cochineal may be discovered by the spectroscope if present in large quantity, but if it amounts to only 12 per cent. of the total coloration it cannot be so detected; it rapidly disappears from the wine, being precipitated in the lees.

*Fuchsine* should be sought for in all such wines as are found to be adulterated with other substances. The reaction (J) of Table B is very sensitive. Great care must be taken to avoid loss of rosaniline from imperfect decomposition of its salts in solution; moreover, arsenic should always be sought for where the wine is found to contain any aniline. Fuchsine rapidly separates from the wines to which it has been added.

A skein of silk becomes dyed rose-red by soaking in a wine adulterated with fuchsine, and its colour passes to yellow on treatment with hydrochloric acid, but to bright rose if the wine was pure. The dyed skein treated with dilute cupric acetate and dried at 100°, becomes fine deep rose-violet colour if fuchsine is present; and of a lilac tinged with ash-grey if the wine is pure. This reaction is very sensitive.

*Portugal berries* (*Phytolacca*).—The rose or lilac colorations of the reactions (A) (G), and especially (C) are very sensitive.

*Althæa rosea*, or *Hollyhock*.—Much used. This substance imparts a peculiar flavour, which in a few months becomes actually disagreeable, while the colouring matter itself very rapidly precipitates.

*Beetroot* is generally employed only to mask other adulterants. The

lilac tint of reaction C of Table A, if the beetroot is fresh and the yellowish colours due to alkalis (reactions D, E, and F) of the same table are very sensitive even with old decoctions.

*Black Elder. Dwarf Elder.*—The dwarf elder communicates a faintly turpentinous odour. The berries of both varieties are particularly used to impart a special colour and flavour to port wine. The *teinte de Fismes*, which is largely used in that town, in Paris, and elsewhere, is made by digesting 250 to 500 parts of elderberries, and 30 to 60 parts of alum with 800 to 600 of water, and then submitting the mixture to pressure. M. Maumené reports having discovered as much as 4 to 7 grams of alum per litre in wines adulterated with this substance. Sometimes (though rarely) the alum is replaced by tartaric acid. Wines adulterated with elder yield a violet-blue lake (reaction H, Table A). By comparison with pure wine the difference is very marked.

A piece of flannel, or skein of silk, mordanted with aluminium acetate, heated for some time in the suspected wine, then washed and immersed in water made faintly alkaline with ammonia, becomes green, if the wine is pure, but dark brown if black elder is present. Probably the same reaction occurs with dwarf elder.

*Privet berries;* very seldom used. The general reactions, particularly (N) and (P) of Table A must be relied on.

*Whortleberries;* very seldom used, and only for the commonest wines. The principal characteristics are given in Table B, L (*c*). In wines suspected to be adulterated with this substance, citric acid should be sought for, its presence being one of the best indications of the adulteration.

*Indigo.*—The reactions A (*b*) and B (*b*) of Table B are so sensitive that they are sufficient alone to characterise indigo.

Wool or silk mordanted with aluminium acetate, heated with 20 to 40 c.c. of the suspected wine, nearly to dryness, washed, and then dipped into very dilute ammonia becomes dirty green if the wine be pure, but blue if a trace of indigo be present. Indigo being often used to mask the too bright colours of cochineal and fuchsine, they should always be sought for after the removal of the indigo by clarification with albumin.

Indigo very rapidly separates from wine, and it may frequently be found in the lees, even when the wine itself gives no indication of its presence.

Substances other than those mentioned are sometimes employed in the adulteration of wines; among them are archil residues, sulphopurpuric and sulphoalizaric acids and their salts, but these have been only recently brought out, and are not yet employed to any great extent. Except in such cases as indigo and cochineal, it is only upon a series of concordant reactions that the presence of an artificial colouring matter should be affirmed.

C. H. P.

### Detection of Fuchsine in Wines. By E. JACQUEMIN (Bull. Soc. Chim. [2], xxvi, 68—71).

THE following processes are given:—

1. *By the direct Dyeing of Gun-cotton.*—A wad of gun-cotton is heated for a few moments in about 20 c.c. of the wine, then withdrawn and washed with water. Fuchsine and archil (which is sometimes used to increase the colour of wines) both dye it, whereas the natural colouring matter of the wine does not. The two former may be differentiated by moistening the dyed wad with ammonia, which changes the archil to violet, and bleaches (though slowly) the fuchsine. Gun-cotton which is undergoing change is more efficacious than that which is new and pure.

Other substances used for artificially colouring wines fix themselves upon gun-cotton sufficiently well for conclusions to be drawn as to their nature by the changes which they undergo on treatment with ammonia.

2. *By the direct Dyeing of Wool.*—Wool is scarcely affected by the natural colouring matter of wine, but is dyed by fuchsine and archil. About 100 c.c. of wine are evaporated till the alcohol is removed. A piece of embroidering wool is then immersed into it, and the evaporation continued till the bulk is reduced one-half, when the wool is withdrawn and thoroughly washed. The tints of fuchsine and archil are slightly modified by the natural colouring matter of the wine, but on treatment with ammonia, the last-mentioned changes to brown, whilst the fuchsine is rapidly dissolved, and the colourless ammoniacal solution becomes red on acidification. The archil becomes violet, as does also the ammonia in which it is dipped.

3. *By Dyeing Wool with Ammoniacal Fuchsine.*—The alcohol is evaporated from 100 or 200 c.c. of the wine, the remainder made alkaline with ammonia, and then shaken with ether. The colourless ethereal solution is evaporated on a piece of white wool as before, which then becomes dyed red as the evaporation proceeds. The destruction of this colour by ammonia, and its reproduction by acetic acid, leave no doubt as to the nature of the colouring matter. If archil be present, the ethereal solution is red.

C. H. P.

## Technical Chemistry.

### Composition of Chinese Porcelain-clay and Glass-ware. By W. KULMANN (Dingl. polyt. J., ccxx, 445—446).

THE samples under investigation were obtained from Kinkiang, in China, in the form of bricks,—a form in which the raw materials are used for the manufacture of porcelain. They had undergone a preliminary washing. Analysis showed that 100 parts of the porcelain-clay dried at 110° contained—

| | I. Quality. | II. Quality. | III. Quality. |
|---|---|---|---|
| Silicic acid (soluble) ..... | 0·504 | 52·208 | 51·210 |
| ,, (insoluble) .... | 50·133 | — | — |
| Alumina ..... | 32·737 | 31·997 | 33·150 |
| Ferric oxide ..... | 0·955 | 0·712 | 0·709 |
| Ferrous oxide ..... | 1·690 | 1·911 | 1·936 |
| Manganous oxide..... | 0·827 | 0·540 | 0·843 |
| Lime ..... | 0·501 | 0·464 | 0·456 |
| Magnesia ..... | 0·268 | 0·273 | 0·284 |
| Potash ..... | 2·520 | 1·560 | 1·403 |
| Soda ..... | traces | 0·970 | 0·992 |
| Loss ..... | 10·011 | 9·499 | 9·500 |

From these analyses it is seen that the clays used are very pure, and consist of a gangue rich in potash.

100 parts of the glass-ware dried at 110°, contained—

| | I. Quality. | II. Quality. |
|---|---|---|
| Silicic acid ..... | 78·09 | 74·19 |
| Alumina ..... | 13·17 | 13·77 |
| Ferric oxide..... | 0·99 | 1·26 |
| Manganous oxide .. | traces | 1·03 |
| Lime..... | 0·74 | 1·50 |
| Magnesia ..... | 0·23 | traces |
| Potash ..... | 2·60 | 3·01 |
| Soda..... | 2·32 | 2·84 |
| Loss ..... | 2·60 | 2·66 |
| | 100·74 | 100·26 |

These glass-masses correspond in their composition with pegmatite. Before use, they are generally mixed with lime.

D. B.

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**Etching on Glass.** By E. SIEGWART (Dingl. polyt. J., ccxx, 479—480).

SINCE hydrofluoric acid can be sold cheaply, it seems to be more and more used for the decoration of glass. This can be easily understood, as glass articles, when sufficiently etched, will have a much better appearance than engravings on glass. The best decorations are obtained by etching several portions of the glass surface with ammonium fluoride slightly acidified with acetic acid. If plates of glass are to have an ice-like lustre, the glass is, in the first place, covered with a layer of very small shot, over which very dilute hydrofluoric acid is then poured. Results similar to etched photographs are obtained by exposing any negative picture on a layer of gum or caoutchouc-layer rendered sensitive by potassium bichromate, and then dusting it with red lead. The red negative thus obtained is fixed as usual, and burnt in, and the more soluble lead glass thus obtained is treated with concentrated nitric acid, whereby a dull white picture is produced, appeairng positive when looked through.

D. B.

## Tin and Lead Alloys used for Household Vessels.

By F. KNAPP (Dingl. polyt. J., ccxx, 446—453).

WITH regard to the estimation of the value of the above alloys for household vessels, &c., two points have to be considered. (1.) Fitness for the manufacture of tin vessels, which depends upon their appearance, colour, and their property of allowing casting and turning. (2.) Resistance to chemical agents, *i.e.*, to the absorption of lead and tin by liquids, provisions, &c. The Acts passed in various countries for protecting the public against the injurious effects of tin and lead alloys, and the numerous scientific investigations, differ very considerably from one another.

For investigation, the alloys are, in the first place, treated under various conditions with dilute acetic acid, with salt-solution, sometimes also with dilute sulphuric acid, and the liquid is tested for lead and tin. The result depends on the metallic mixture, the strength and temperatures of the reagents, but chiefly, also, on the extent of surface which the alloy offers to the acting liquid. This latter very important circumstance seems to be generally neglected by chemists.

Pohl mentions that certain alloys rich in lead (5 parts tin and 12 parts lead) offer the same resistance to acetic acid as alloys rich in tin. Phlo recommends an alloy, consisting of 4 parts tin and 9 parts lead, which, he says, possesses all the advantages of alloys rich in tin, and is not attacked by vinegar or salt water. These two alloys appear to have nearly the same composition.

| | Pohl. | Phlo. |
|---|---|---|
| Tin..... | 5 parts = 30·77 p. c. | 4 parts = 29·74 p. c. |
| Lead .... | 12 parts = 69·23 „ | 9 parts = 70·26 „ |

These alloys exhibit, indeed, the character of a chemical compound, their resistance to chemical agents being due to the intimate union of the constituents. In fact—

3Sn = 177 correspond with 29·95 per cent.
4Pb = 414 „ „ 70·05 „

but Riche (1863, 170, 113) mentions that between tin and lead only one chemical combination, viz., $Sn_2Pb$, exists, which corresponds with the maximum of the contraction between the two metals.

For investigation, the author prepared the following alloys:—

*A*. 4 parts of tin with 9 parts of lead.
*B*. 4 parts of tin with 15 parts of lead. (Acc. to $SnPb_2$.)
*C*. 4 parts of tin with 1 part of lead.

The evident tendency which alloys generally (more especially tin-lead alloys) possess of separating before cooling, necessitated a determination of the fused mixtures. After fusion, portions of *A* and *B* were analysed when cold. They were found to be in conformity with the calculated percentages of the above proportions of lead and tin; the two metals had, therefore, not been re-separated in any way. Moreover, they were found to allow of casting, rolling, and turning, although the alloy *C* was somewhat tough.

1. *Behaviour to Distilled Water.*—Strips of plate were allowed to remain in distilled water for several days. *A* remained unaltered. *B* and *C* were attacked, depositing oxide. It was, however, noticed that in the case of the latter alloys their surface was not attacked regularly, but that the action had proceeded principally from rough places. The consistence of the surface seemed, therefore, to exert an influence on their behaviour, and made it necessary to repeat the experiment in a different manner. It was found that the alloy *A*, which, in the first experiment, was smooth and polished, was strongly attacked when in the second experiment it was left in the water with a rough surface. *B* when polished was less acted upon.

2. *Action of Vinegar*—

| | thick. | wide. | high. |
|---|---|---|---|
| Alloy A..... | 0·15 cm. | 8·2 cm. | 14·8 cm. |
| „ B..... | 0·15 „ | 7·4 „ | 13·8 „ |
| „ C..... | 0·15 „ | 8·2 „ | 14·0 „ |

The clean-scraped plates (not polished) were placed in a glass vessel under vinegar (commercial 3·078 p.c.), and left alone for 7 days in a cold room (1—7 December). The vinegar was then poured off, and saturated with sulphuretted hydrogen. *A*, *B*, and *C* gave precipitates differing in volume and colour. Precipitate of *A* was smaller than of *B* and *C*. Colour of *C* was yellowish-brown, of *A* and *B* blackish-brown.

For a quantitative determination, the same plates were cleaned and placed in 1·25 litres of vinegar (4 p.c.), but were occasionally taken out of the liquid, exposed to the air, and again put in. After a week, the clear liquids were poured off, precipitated by sulphuretted hydrogen, the lead determined as sulphate, and the tin as oxide. Obtained—

| | Lead. | Tin. | Total. |
|---|---|---|---|
| Alloy A.... | 0·1622 g. | 0·0639 g. | 0·2261 g. |
| „ B.... | 0·1957 „ | 0·0334 „ | 0·2291 „ |
| „ C.... | 0·0063 „ | 0·0796 „ | 0·0832 „ |

In the following experiment, the action took place at a boiling heat. The same plates were used. After cleaning with emery-powder and washing, they were placed under vinegar (4·5 p.c.), and boiled for an hour. Analyses of the liquids showed that the effect of high temperatures was considerably lower than that which time produced.

3. *Behaviour to Salt-solution.*—The spec. grav. of the solution was 1 025, containing 3·5 p.c. of salt. The plates were left in this solution for seven days in a cold room. *B* contained only traces; *C*, a large deposit. *A* showed a deposit. The analyses of the deposits showed nothing but lead. The same experiment was repeated with solutions at a temperature of blood-heat, and gave the same results. The third experiment was made by boiling the plates with the solutions for an hour, when deposits were obtained containing lead and tin, whereas the solutions were free from both. Alloy *A* contained 9 times more lead than alloy *B*, but gave to vinegar not 9, but 26 times more lead; *B*, *vice versâ*, lost in a salt solution over 21 times more lead than *A*.

In conclusion, the author states that the quantity of the metals dissolved is, even under the intentionally unfavourable conditions of the experiments, not very considerable, and for the most part hygienically unimportant under the conditions of ordinary life.

D. B.

## Extraction of Silver by the Moist Way.

By A. GUYARD (Bull. Soc. Chim., xxv., 6—8).

THE silver-ores of Bolivia, known by the name of *Rossicler*, have the following composition :—

| | | | |
|---|---|---|---|
| Sulphur | 18·35 | 16·20 | 17·85 |
| Silver | 48·15 | 46·10 | 38·10 |
| Antimony | 10·85 | 7·10 | 28·35 |
| Iron | 5·60 | 7·70 | 0·95 |
| Zinc | 4·50 | 4·10 | 5·25 |
| Bismuth | 2·20 | — | — |
| Lead | trace | trace | 1·50 |
| Arsenic | 0·15 | 0·10 | 0·25 |
| Copper | — | — | 0·25 |
| Chlorine | — | 0·15 | — |
| Gangue | 10·20 | 18·55 | 7·50 |
| | 100·00 | 100·00 | 100·00 |

These ores cannot be treated in the dry way, but the silver is easily extracted by heating the finely powdered ore with four to five times its weight of sulphuric acid until it is converted into a pasty cream-coloured mass. The sulphates are extracted with water, and the silver precipitated with iron or copper. The precipitate contains antimony and 90—92·5 per cent. of silver; it is purified by fusing with nitre. The residue, consisting chiefly of gangue, contains 2·5—3 per cent. of silver as chloride and antimonite, and must be treated like other poor silver ores.

On heating the ore with sulphuric acid, a large quantity of sulphur sublimes, carrying with it a not inconsiderable proportion of silver, which is easily isolated by roasting.

C. S.

## Production of Metallic Films on the Surface of Organic Substances for the purpose of Electro-deposition.

By P. CAZENEUVE (Compt. rend., lxxxii, 1341—1342).

THE author proposes the following method of treating objects intended to receive a deposit of metals, in order to render them conductors of electricity. The object is first immersed in a 10 per cent. solution of silver nitrate in methyl alcohol, to which 3 per cent. of nitric acid is added, and allowed to remain for a longer or shorter time according to the nature of the object. It is then drained, partially dried by rapid motion, and while still moist placed for a few seconds in a saturated solution of ammonia, after which it is dried at a low

temperature. Lastly, it is suspended above the surface of mercury heated by means of boiling water. A few minutes' exposure to the mercurial vapour suffices to reduce the double nitrate of silver and ammonia formed by the previous treatment, the object becoming completely covered with a metallic film.

Leaves, flowers, insects, and other organic objects thus treated take a regular deposit of copper. The method is said to be safer and more rapid than those in which the hydrogen-compounds of arsenic, phosphorus, and sulphur, or solutions of phosphorus in carbon bisulphide, are employed as reducing agents.

J. R.

**Manufacture of Archil-extract and Archil-dough.** By SEROZ and CHOGNARD (Dingl. polyt. J., ccxx, 480).

SEROZ and Chognard's method consists in macerating the lichens for a quarter of an hour in water to which a small quantity of potash is added, and heating in closed vessels to 100°—120° by means of steam of several atmospheres of pressure. The object of applying heat is to convert the acids quickly and completely into orcïn. The clear liquid is separated from the insoluble woody mass and concentrated by evaporation. The concentrated solution is then treated with ammonia, brought into an iron or wooden vessel, and oxygen introduced into the latter. Thus the formation of orcïn takes place much more quickly than is usually the case when the orcïn is oxidised by the air.

To obtain archil-dough, a quantity of extracted lichens is added to the above concentrated solution, treated with ammonia until the mixture assumes a thick pasty form, and oxygen is then introduced. The oxidising vessels are provided with an agitator, so that all portions of the dough are brought into contact with the oxygen.

D. B.

**Saponification of Neutral Fats in Autoclaves.** By F. NITSCHE (Dingl. polyt. J., ccxx, 459—461).

The author has conducted a large number of autoclave operations in which all the stages are examined by analysis, and he has found the following method to give sufficiently accurate results for comparing the different stages of the production. A sample is drawn from a cock fixed into the autoclave, and a weighed quantity boiled with a proportionately calculated quantity of sulphuric acid of certain specific gravity. The acid thus obtained is washed with water, and 10 grams are dissolved in 500 grams of alcohol (96 p. c.) on a water-bath, using cylindrical bottles for the solution. When the substance is completely dissolved, the bottle is corked up and put into a cold place. The neutral fats thus separate in flocculent masses, which are filtered, washed with cold alcohol, dissolved in ether, and evaporated on a tarred glass.

The following table gives a series of results, which show the

differences obtained in this process, and which give the value of the sample for examination of other manufacturing products:—

| Samples. | | | | Neutral fat. | Remarks. |
|---|---|---|---|---|---|
| Hours. | At. | Reagents. | | Per cent. | |
| 7 | 8–9 | 3 p. c. lime | | 15·270 | Melting-point of fatty acid, 39°. |
| 8 | „ | 3 „ | | 5·520 | Ditto, 44°. |
| 9 | „ | 3 „ | | 0·812 | Ditto, 45°. |
| 6 | „ | 3 „ | | 2·880 | Proportionately decreasing turbidities. |
| 7 | „ | 3 „ | | ? | |
| 8 | „ | 3 „ | | ? | |
| 9 | „ | 3 „ | | 0·340 | |
| 7 | „ | 1 „ | | 1·660 | Proportionate turbidities. |
| 8 | „ | 1 „ | | 0·905 | |
| 9 | „ | 1 „ | | 0·542 | |
| 16 | „ | Water alone | | 2·500 | Successively smaller turbidities. |
| 7 | „ | „ | „ | 1·796 | |
| 8–11 | „ | „ | „ | ? | |
| 12 | „ | „ | „ | 0·660 | |
| 12 | „ | „ | „ | 0·896 | Palm oil. |
| 12 | „ | „ | „ | 1·350 | ⅓ tallow and ⅔ palm oil. |
| 12 | „ | 1 p. c. sulphuric acid | | 2·800 | Since these results were not satisfactory, and it was feared that the apparatus might be injured, no further experiments were made with sulphuric acid. |
| 14 | „ | 1 „ | „ | 1·290 | |
| 17 | „ | 1 „ | „ | 0·960 | |
| 21 | „ | 1 „ | „ | 0·400 | |
| 12 | „ | Water alone | | 2·620 | |
| 14 | „ | „ | „ | 0·864 | |
| 14 | „ | 2 p. c. sulphuric acid | | 1·350 | |
| Fatty acid of distillation | | | | — | No signs of separation after eight days. |
| Tallow agitated with 6 p. c. concentrated sulphuric acid at 135° for 1 hour | | | | 25·498 | |
| Fatty acid | | | | 1·815 | |
| Fatty acid agitated at 105° with 2 p. c. sulphuric acid | | | | 1·024 | |
| Fatty acid agitated at 121° with 2 p. c. sulphuric acid | | | | 0·688 | |
| Fat from filter-presses | | | | 2·150 | |
| Two fatty acids (obtained according to Bok's method) | | | | — | No separation. |

D. B.

# PAPERS READ BEFORE THE CHEMICAL SOCIETY.

## XVIII.—*On Hypovanadic Oxide (Vanadium Tetroxide), and its Compounds.*

By J. K. Crow (Student in the Chemical Laboratory of Owens College, Manchester).

Hypovanadic oxide was first prepared by Berzelius (*Pogg. Ann.*, xxii, 1), who also at the same time described some of its compounds. The new light which has lately been thrown on the constitution of the vanadium compounds by Roscoe's researches, seemed to render another and more complete investigation of the compounds of hypovanadic oxide desirable.

At the commencement of this investigation, the experiment described in Roscoe's researches as to the effect of various reducing agents on acid solutions of vanadium pentoxide was repeated, and the same results were obtained as are therein described.

Hypovanadic oxide can be prepared in solution by the action of sulphurous acid, hydrogen sulphide, or oxalic acid on acid solutions of the pentoxide. Berzelius showed, in the paper above referred to, that hypovanadic oxide is capable of acting both as an acid and as a base, and described the mode of preparation of some of its salts, without, however, giving any analyses.

In all the following analyses of the hypovanadic salts, the vanadium was estimated either volumetrically by titration with standard potassium permanganate solution, or by weighing the pentoxide after fusion.

### I. *Hypovanadic Oxide and Hydrate.*

(1.) Hypovanadic oxide can be obtained, not only by the slow oxidation of the trioxide in the air, as described by Roscoe, but likewise by heating the chloride, about to be described, to redness, in an atmosphere of carbon dioxide. Prepared by the latter method, the oxide contains only a small proportion of vanadic acid, as the following analyses of two preparations show:—(*a*.) 0·301 gram of the oxide required 35·5 c.c. of $KMnO_4$ solution (1 c.c. = 0·008036 $V_2O_4$), giving 92·6 p.c. of $V_2O_4$; and (*b*) weight of oxide taken, 0·1825 gram required 21·3 c.c. of $KMnO_4$ solution, corresponding to 95·6 p.c. of $V_2O_4$.

The oxide thus obtained appears as a dark green amorphous powder, insoluble in water, but readily soluble in alkalis or in acids. When kept in loosely stoppered bottles, it gradually absorbs oxygen from the air, with formation of the highest oxide. This fact is shown by the analyses of two specimens of hypovanadic oxide which were prepared, some years ago, on the dates given below :—

| | Preparation A. | | Preparation B. | |
|---|---|---|---|---|
| | Dec. 3, 1875. | July 6, 1876. | Dec, 3, 1875. | July, 6, 1876. |
| $V_2O_4$ ..... | 48·09 | 45·44 | 29·61 | 19·91 |
| $V_2O_5$ ..... | 42·45 | 43·67 | 55·11 | 63·41 |
| $H_2O$ (by difference) .. | 9·46 | 10·89 | 15·28 | 16·68 |
| | 100·00 | 100·00 | 100·00 | 100·00 |

Anhydrous hypovanadic oxide may also be prepared by heating in an atmosphere of carbon dioxide the hydrate about to be described.

(2.) *Hypovanadic Hydrate.*—This body is obtained, as Berzelius describes, from a solution of the sulphate or chloride of hypovanadic oxide, by cautious precipitation with a cold solution of sodium carbonate, added drop by drop, till the supernatant liquid, after the greyish-white precipitated hydrate has subsided, is colourless; excess of the precipitant dissolves some of the hydrate, and the liquid is then coloured brown; whereas if sufficient carbonate of soda has not been added, the solution is blue. As the hydrate absorbs oxygen from the air very rapidly, it must be filtered off in an atmosphere of carbon dioxide and dried in the filter-paper on a porous plate over sulphuric acid in a vacuum; thus prepared, hypovanadic hydrate is a black amorphous mass, exhibiting, when broken, a glassy fracture. It is insoluble in water, but dissolves readily in acids or alkalis. Two preparations were made and analysed with the following results :—

*Preparation A.*—Weight taken = 0·8736 gram. $H_2O$ obtained = 0·3758 gram. 0·3910 gram required 79·5 c.c. $KMnO_4$ for oxidation. (1 c.c. = 0·00806 gram $V_2O_4$.)

*Preparation B.*—Weight taken = 0·4565. $H_2O$ obtained = 0·1960 gram. 0·3354 gram required 23·8 c.c. $KMnO_4$ solution.

| | Found. | | | Calculated for $V_2O_4 + 7H_2O$. |
|---|---|---|---|---|
| | A. | B. | Mean. | |
| $V_2O_4$ ..... = | 56·68 | 57·17 | 56·92 | 56·88 |
| $H_2O$ ..... = | 42·90 | 42·94 | 42 92 | 43·12 |
| | 99·58 | 100·11 | 99·84 | 100·00 |

On heating hypovanadic hydrate for some time at 100° in a current of carbon dioxide, it loses four molecules of water; thus one experiment gave the following results:—0·332 gram of the hydrate was heated at 100°, till it remained constant; it had then lost 0·080 gram of $H_2O$ or 24·09 p.c.: the calculated amount from the loss of four molecules of water being 24·65 p.c.

When dissolved in acids, hypovanadic oxide yields the hypovanadic salts, whilst with alkalies it forms the hypovanadates.

### II. *Hypovanadic Sulphates.*

I. Trisulphate, $V_2O_4.3SO_3 + 6H_2O$.—Pure vanadic oxide is dissolved in concentrated sulphuric acid and the solution reduced with sulphurous acid. On evaporating the resulting blue solution over a water-bath, a light blue crystalline mass is left behind; this is partially freed from adhering sulphuric acid by drying on a porous tile, and then washed with ether till the washings are no longer acid; the mass is finally dried by pressure between filter-paper. Hypovanadic trisulphate thus prepared is a light blue crystalline powder. Three preparations gave, on analysis, the following numbers:—

(1.) Weight taken = 0·321 gram. $BaSO_4$ obtained = 0·4401 gram: 0·299 gram substance yielded 0·104 gram $V_2O_5$, and 0·404 gram gave 0·084 gram $H_2O$.

(2.) 0·311 gram salt yielded 0·425 gram $BaSO_4$; 0·3070 gram required 12·4 c.c. $KMnO_4$ solution. (1 c.c. = 0·0080016 $V_2O_4$), and 0·431 gram gave 0·091 gram $H_2O$.

(3.) 0·576 gram substance gave 0·774 gram $BaSO_4$; also 0·6545 gram required 26·4 c.c. $KMnO_4$ solution. (1 c.c. = 0·00806 $V_2O_4$.)

The results obtained show the formula of this body to be $V_2O_4.3SO_3 + 6H_2O$.

| | Found. | | | | Calculated. |
|---|---|---|---|---|---|
| | A. | B. | C. | Mean. | |
| $V_2O_4$ ..... | 32·05 | 32·31 | 32·51 | 32·29 | 32·37 |
| $SO_3$ ..... | 47·12 | 46·92 | 46·14 | 46·73 | 46·63 |
| $H_2O$..... | 20·79 | 21·14 | — | 20·95 | 21·00 |
| | 99·96 | 100·37 | — | 99·97 | 100·00 |

(2.) Another hydrated trisulphate, having the composition $V_2O_4.3SO_3 + 4H_2O$, has recently been described by Gerland. It is prepared by precipitating a concentrated aqueous solution of any hypovanadic sulphate with strong sulphuric acid.

Both trisulphates are light blue crystalline powders, which deliquesce in the air, forming a blue syrup. The latter, on long exposure to the air, deposits beautiful blue stellate crystals, which have not been obtained in sufficient quantity for analysis. The crystalline powders dissolve only slowly in cold water, but quickly in hot; they are insoluble in ether, and scarcely soluble in absolute alcohol.

(3.) *Hypovanadic Disulphates*, No. 1. $V_2O_4.2SO_3 + 7H_2O$.—Either the pure trisulphate, or the residue left on evaporation of a solution of $V_2O_4$ in sulphuric acid, is treated with absolute alcohol; the mass swells considerably and is allowed to settle, and the alcohol is poured off; after repeated treatment with absolute alcohol till no more acid is removed, the sulphate is at once transferred to a filter, the alcohol drained off, and the mass quickly dried between filter-paper. Analyses of two different preparations gave the following numbers:—

*Preparation* 1.—Weight of salt taken = 0·0249 gram; $BaSO_4$ obtained 0·260 gram. Number of c.c. of $KMnO_4$ solution used = 11·4 (1 c.c. = 0·0080016 $V_2O_4$), also 0·3455 gram substance yielded 0·097 gram $H_2O$.

*Preparation* 2.—0·373 gram of salt gave 0·387 gram $BaSO_4$. 0·256 gram yielded 0·104 gram $V_2O_5$; and from 0·410 gram substance, 0·115 gram of $H_2O$ was obtained.

| | Found. | | | Calculated. |
|---|---|---|---|---|
| | 1. | 2. | Mean. | |
| $V_2O_4$ ..... | 36·60 | 36·84 | 36·72 | 36·81 |
| $SO_3$ ..... | 35·58 | 35·30 | 35·44 | 35·35 |
| $7H_2O$..... | 28·08 | 28·05 | 28·06 | 27·84 |
| | 100·26 | 100·19 | 100·22 | 100·00 |

This disulphate is a deliquescent light blue powder. Its aqueous solution does not deposit crystals when evaporated to dryness, but leaves a gummy mass, and if evaporated slowly over sulphuric acid, it undergoes decomposition, an insoluble oxide being precipitated.

No. 2. $V_2O_4.2SO_3 + 4H_2O$.—A second disulphate, having the above composition, was prepared by Berzelius by allowing the residue above described to stand in contact with absolute alcohol for several hours. The following are the analytical results obtained in confirmation of the results of Berzelius:—

| | | | | | | Calculated. |
|---|---|---|---|---|---|---|
| 0·421 gram substance | gave 0·1925 gram | $V_2O_5$ | or p.c. of | $V_2O_4$ | = 41·48 | 41·70 |
| 0·230 „ „ | „ 0·2681 „ | $VaSO_4$ | „ | $SO_3$ | = 40·06 | 40·21 |
| 0·280 „ „ | „ 0·0235 „ | $H_2O$ | „ | $H_2O$ | = 18·22 | 18·09 |
| | | | | | 99·76 | 100·00 |

According to Gerland, the above method yields a trisulphate; but it appears probable that he did not wash the salt with alcohol sufficiently long to remove all the sulphuric acid.

In determining the percentage of water in the above sulphates, the substances were heated in a tube with lead oxide, and the water weighed by collecting it in a calcium chloride tube. This method is rendered necessary by the fact that these sulphates do not give off the whole of their water till they begin to decompose, and hence the water cannot be determined by simple loss of weight.

### III. *Hypovanadic Chloride*, $V_2O_4Cl_2 + 5H_2O$.

This substance is prepared by dissolving pure vanadium pentoxide in strong hydrochloric acid; chlorine is given off on the application of heat, and the green solution thus obtained is reduced with hydrogen sulphide: after filtering off the precipitated sulphur, the resulting blue liquid is evaporated to dryness over a water-bath; a brown amorphous deliquescent residue is left behind, which yields a blue solution with water, and a brown one with absolute alcohol or fuming hydrochloric acid. The singular fact that certain blue solutions of vanadium yield, on evaporation, a brown residue, has already been noticed by Roscoe. In this case, the change of colour is certainly not due to a different state of oxidation, since when the chloride is dissolved either in absolute alcohol or in strong hydrochloric acid in an atmosphere of carbon dioxide, the brown solution obtained changes directly to blue on the addition of a few drops of water freed from air. This seems to point to the conclusion that only a certain hydrate of hypovanadic chloride is brown, namely, that which is left on evaporation of the chloride solution over a water-bath, and that when

this body passes into a higher state of hydration, its colour changes from brown to blue.

The analyses of two different preparations gave the following results:—

*Preparation* 1.—0·635 gram of the substance required 35·8 c.c. of $KMnO_4$ solution (1 c.c. = 0·008036 gram $V_2O_4$). 0·2615 gram gave 0·383 gram AgCl and 0·008 gram Ag.

*Preparation* 2.—0·742 gram substance yielded 0·368 gram $V_2O_5$. 0·277 gram gave 0·397 gram AgCl and 0·0155 gram Ag.

| | Found. | | | Calculated. |
|---|---|---|---|---|
| | 1. | 2. | Mean. | |
| $V_2O_4$ | 45·30 | 45·26 | 45·28 | 45·35 |
| HCl | 38·31 | 38·32 | 38·32 | 39·89 |
| $H_2O$ | — | — | — | 14·76 |
| | — | — | — | 100·00 |

The loss of more than 1 per cent. of chlorine is probably due to a partial decomposition of the chloride at 100°, and this is confirmed by the fact that, after heating for some time at that temperature, it becomes no longer entirely soluble in water.

## IV. *The Hypovanadates.*

The power which hypovanadic oxide possesses of uniting with bases to form the salts known as hypovanadates, has already been pointed out. Berzelius described the formation of the potassium and ammonium salts, but does not appear to have analysed them. The hypovanadates of the alkalis are soluble in water, and the rest are insoluble, and obtained by double decomposition.

(1.) *Potassium Hypovanadate*, $(V_2O_4)_2.K_2O + 7H_2O$.—To obtain this compound, a moderately concentrated solution of hypovanadic chloride or sulphate is treated with excess of caustic potash, and the whole transferred to a stoppered bottle just large enough to hold the mixture, and allowed to stand a few hours; the dark brown solution thus obtained deposits the potassium-salt either as reddish-brown brilliant crystalline scales, or as slender needle-shaped crystals aggregated in tufts. The salt is transferred to a filter and washed with potash solution till free from hydrochloric or sulphuric acid, then with dilute alcohol, containing a little acetic acid, to dissolve out any adhering carbonate of potash, and finally with alcohol alone; it is

then pressed between filter-paper till dry. The salt thus obtained is a dark brown crystalline mass, permanent in the air; it is very soluble in water, but scarcely so in potash solution, and insoluble in alcohol. The aqueous solution of this salt is dark brown, and is gradually decolourised on standing in the air, owing to the oxidation of the hypovanadic acid. The following results were obtained in the analysis of two different preparations:—

*Preparation* 1.—Weight taken = 0·246. Weight of $K_2SO_4$ obtained = 0·080 gram. 0·2054 gram of the salt required 15·3 c.c. $KMnO_4$ solution. (1 c.c. = 0·00806 gram $V_2O_4$.) 0·235 gram salt yielded 0·539 gram $H_2O$.

*Preparation* 2.—Weight taken = 0·6373 gram. Weight of $K_2SO_4$ obtained = 0·1988 gram. 0·2332 gram salt required 17·4 c.c. of $KMnO_4$ solution.

| | Found. | | | Calculated for $(V_2O_4)_2.K_2O + 7H_2O$. |
|---|---|---|---|---|
| | A. | B. | Mean. | |
| $V_2O_4$ ..... | 60·03 | 60·14 | 60·08 | 60·25 |
| $K_2O$ ..... | 17·40 | 16·95 | 17·17 | 16·99 |
| $H_2O$ ..... | 22·94 | — | 22·94 | 22·76 |
| | 100·37 | — | 100·19 | 100·00 |

(2.) *Sodium Hypovanadate*, $(V_2O_4)_2.Na_2O + 7H_2O$, prepared in a similar way to the potassium salt, is obtained in brown crystalline scales, which possess the same properties as the potassium compound. They are very soluble in water, but scarcely soluble in caustic soda solution. The salt has a composition similar to that of the potassium salt, and, as the following analysis shows, may be represented by the above formula:—

Weight of salt taken = 0·1899 gram: required 15·1 c.c. $KMnO_4$ solution (1 c.c. = 0·00806 gram $V_2O_4$). Weight of $H_2O$ obtained = 0·0461 gram.

Also 0·4773 gram salt yielded 0·1323 gram $Na_2SO_4$; and in another preparation 0·2994 gram salt required 24·05 c.c. $KMnO_4$ solution (1 c.c. = 0·007954 $V_2O_4$).

| | Found. | | | Calculated. |
|---|---|---|---|---|
| | A. | B. | Mean. | |
| $V_2O_4$ ..... | 63·82 | 64·06 | 63·94 | 63·93 |
| $Na_2O$ ..... | 12·10 | — | 12·10 | 11·89 |
| $H_2O$ ..... | 24·27 | — | 24·27 | 24·18 |
| | 100·19 | — | 100·31 | 100·00 |

(3.) *Ammonium Hypovanadate*, $(V_2O_4)_2.(NH_4)_2O + 3H_2O$.—This salt is obtained, as the potassium and sodium salts, by precipitating a solution of hypovanadic sulphate or chloride with ammonia in excess. A brown crystalline precipitate of ammonium hypovanadate is formed, which is washed quickly with ammonia and then with alcohol and acetic acid, in the same manner as the potassium salt: it is finally dried in a vacuum over sulphuric acid, as it oxidises rather readily in the air. It is then obtained as a dark brown crystalline mass, soluble in water, forming a nearly black solution, and reprecipitated on addition of ammonia.

In the following analyses the ammonia was determined by distilling the salt with caustic potash solution, and passing the ammonia into a certain volume of decinormal hydrochloric acid. The quantity of non-saturated acid was then determined with standard soda solution.

*Preparation* 1.—Weight taken = 0·2545 gram. Weight of $V_2O_5$ obtained = 0·212 gram. 0·696 gram substance saturated 33·2 c.c. decinormal acid.

*Preparation* 2.—0·1735 gram required 16·35 c.c. $KMnO_4$ solution (1 c.c. = 0·00806 gram $V_2O_4$). 0·223 gram saturated 10·5 c.c. decinormal acid.

| | Found. | | | Calculated for $(V_2O_4)_2.(NH_4)_2O + 3H_2O$. |
|---|---|---|---|---|
| | 1. | 2. | Mean. | |
| $V_2O_4$ ..... | 12·51 | 12·24 | 12·38 | 11·82 |
| $(NH_4)_2O$ ... | 75·99 | 76·07 | 76·04 | 75·86 |
| $H_2O$ ..... | — | — | — | 12·32 |
| | — | — | — | 100·00 |

(4.) *Barium Hypovanadate* $(V_2O_4)_2.BaO + 5H_2O$.—When caustic baryta is added to a solution of hypovanadic chloride till an alkaline reaction is produced, a yellowish-brown precipitate of barium hypo-

vanadate falls down. This is washed from excess of baryta by decanting several times with hot water, and finally washing on a filter. The precipitate is then dried (best in an atmosphere of carbon dioxide) at about 120°. Thus prepared it is a brown amorphous mass, easily soluble in nitric or hydrochloric acid. The following results were obtained in the analysis of this compound:—

*Preparation* 1.—Weight taken = 0·3637 gram. Weight of $BaSO_4$ obtained = 0·147 gram. 0·208 gram required 14·9 c.c. $KMnO_4$ solution (1 c.c. = 0·00806 gram $V_2O_4$).

*Preparation* 2.—Weight taken = 0·4585 gram: required 33·6 c.c. $KMnO_4$ solution, of which 1 c.c. = 0·007954 gram $V_2O_4$. Also 0·360 gram yielded 0·145 gram $BaSO_4$.

| | Found. | | | Calculated for $(V_2O_4)_2.BaO + 5H_2O$. |
|---|---|---|---|---|
| | 1. | 2. | Mean. | |
| BaO | 26·54 | 26·35 | 26·44 | 26·56 |
| $V_2O_4$ | 57·73 | 58·28 | 58·01 | 57·81 |
| $H_2O$ (by difference) | 15·73 | 15·37 | 15·55 | 15·63 |
| | 100·00 | 100·00 | 100·00 | 100·00 |

(5.) *Lead Hypovanadate*, $V_2O_4.PbO$.—This body is precipitated when a solution of lead acetate is added to a solution of potassium hypovanadate. It contains more base in proportion than the potassium compound: hence free acetic acid is formed in the above reaction according to the equation—

$$(V_2O_4)_2.K_2O + 2Pb(C_2H_3O_2)_2 + H_2O = 2KC_2H_3O_2 + 2(V_2O_4.PbO) + 2(C_2H_3O.HO).$$

When nitrate of lead is used instead of acetate, the free nitric acid formed dissolves some of the hypovanadate, and a blue solution is formed. Lead hypovanadate is a brown curdy precipitate, when prepared in the above way. It was dried in an atmosphere of carbon dioxide at 100°. Two preparations of the compound were made and analysed, with the following results:—

*Preparation* 1.—Weight taken = 0·3635 gram: required 19·4 c.c. $KMnO_4$ solution (1 c.c. = 0·00806 gram $V_2O_4$), and yielded 0·2823 gram $PbSO_4$.

*Preparation* 2.—Weight taken = 0·4469 gram, which required 23·7 c.c. $KMnO_4$ solution, and gave 0·3943 gram $PbSO_4$.

| | Found. | | | Calculated for $V_2O_4.PbO$. |
|---|---|---|---|---|
| | 1. | 2. | Mean. | |
| $V_2O_4$ ..... | 43·01 | 42·74 | 42·87 | 42·77 |
| PbO..... | 57·15 | 57·49 | 57·32 | 57·23 |
| | 100·16 | 100·23 | 100·19 | 100·00 |

(6.) *Silver Hypovanadate*, $V_2O_4.Ag_2O$.—This compound is prepared by precipitating potassium hypovanadate with silver nitrate. It is a black crystalline powder, and contains relatively more base than the potassium salt: hence some free nitric acid is formed in this reaction, which dissolves part of the hypovanadate, forming a blue solution. The reaction may be represented by this equation—

$$(V_2O_4)_2.K_2O + 4AgNO_3 + H_2O = 2(V_2O_4.Ag_2O) + 2KNO_3 + 2HNO_3.$$

Two specimens of the compound were prepared and dried in carbon dioxide at 100°. On analysis they yielded the following results:—

*Preparation* 1.—Weight of salt taken = 0·2272 gram: required 11·7 c.c. of $KMnO_4$ (1 c.c. = 0·00806 gram $V_2O_4$), and gave 0·1433 gram AgCl and 0·0150 gram Ag.

*Preparation* 2.—Weight of salt taken = 0·310 gram: required 16·2 c.c. of $KMnO_4$ solution. 0·3338 gram yielded 0·2285 gram AgCl and 0·0078 gram Ag.

| | Found. | | | Calculated for $V_2O_4.Ag_2O$. |
|---|---|---|---|---|
| | 1. | 2. | Mean. | |
| $V_2O_4$ ..... | 41·51 | 42·12 | 41·81 | 41·86 |
| $Ag_2O$ .. ..... | 58·19 | 58·08 | 58·13 | 58·14 |
| | 99·70 | 100·20 | 99·94 | 100·00 |

# XIX.—*On some Compounds of Antimony Pentachloride with Alcohols and with Ether.*

By W. Carleton-Williams, Assistant-Lecturer on Chemistry, Owens College.

When organic bodies are brought in contact with antimony pentachloride, an energetic reaction generally takes place. The pentachloride splits up into chlorine and antimony trichloride, and the organic matter is either chlorinated by the free chlorine or completely charred by the dehydrating action of the pentachloride. Under suitable conditions it is possible, however, to obtain direct addition-compounds of antimony pentachloride with different alcohols and with ether.

In order to prepare these substances, I first made a considerable quantity of antimony pentachloride by slowly distilling pure crystalline antimony trichloride in a current of chlorine; the product was purified by redistillation.

## 1. $SbCl_5.C_2H_6O$. *Antimony Pentachloride Ethyl Alcoholate.*

Absolute ethyl alcohol, dried over baryta, is added in small portions at a time to antimony pentachloride contained in a wide glass tube surrounded by cold water. As much heat is generated on mixing the two liquids, it is advisible to pour the alcohol gently down the side of the tube, so that it may float on the surface of the pentachloride. The addition of alcohol is continued until no further action takes place. If the operation has been successfully carried out, no gases will be given off, and the contents of the tube will consist of a crystalline body, and a small quantity of unchanged alcohol; but if the alcohol is added too quickly, or if the mixture is not well cooled, the contents of the tube blacken and hydrochloric acid gas escapes.

The ethyl alcoholate is a white crystalline hygroscopic body. It is at once decomposed by water, with formation of alcohol and antimonic acid. In an aqueous solution of tartaric acid it is readily soluble, and it dissolves freely in alcohol, ether, and chloroform. It can easily be obtained in a state of purity by recrystallisation from alcohol; the hot saturated alcoholic solution deposits on cooling beautiful white needle-shaped crystals (sometimes an inch long) which apparently belong to the rhombic system. Unfortunately this substance cannot be preserved even in sealed tubes. A splendid specimen I prepared four months ago has gradually lost its original white colour and assumed a brown tint.

The pure crystals melt at 66°—67° C.; they cannot be distilled without undergoing complete decomposition.

In order to analyse the substance, it was dissolved in tartaric acid and the antimony precipitated as sulphide. A portion of the dried sulphide was gently heated in a stream of carbon dioxide. The chlorine was estimated in the filtrate from the antimony sulphide, after oxidising the sulphuretted hydrogen with potassium permanganate. Or the original substance was repeatedly treated with boiling solutions of sodium carbonate, the precipitated antimony oxide filtered off, and the chlorine estimated in the filtrate.

The carbon and hydrogen were determined in the ordinary way by combustion with copper oxide and lead chromate.

| Weight of substance. | Weight of $Sb_2S_3$ dried at 100° C. | | | $Sb_2S_3$ dried in $CO_2$. | |
|---|---|---|---|---|---|
| 0·584 gram | 0·3475 | of which 0·2874 gave | | 0·2414 | = 35·86 p.c. Sb |
| 0·7275 „ | 0·431 | „ 0·4111 | „ | 0·3463 | = 35·83 „ |

| | Weight of AgCl. | Weight of Ag. | | | |
|---|---|---|---|---|---|
| 0·4458 „ | 0·8933 | 0·0176 | — | — | = 50·87 Cl |
| 0·7275 „ | — | 1·121 | — | — | = 50·66 „ |
| 0·3172 „ | $CO_2$ formed | 0·071, $H_2O$ formed | | 0·0568 | = 6·1 C. 1·98 H. |
| 0·4568 „ | „ | 0·1057 | „ | 0·0751 | = 6·31 C. 1·6 H. |

| | Calculated for $SbCl_5.C_2H_6O$. | Found (mean). |
|---|---|---|
| Sb ..... | 35·31 | 35·84 |
| $Cl_5$ ..... | 51·38 | 50·77 |
| $C_2$ ..... | 6·95 | 6·21 |
| $H_6$ ..... | 1·73 | 1·79 |
| O ..... | 4·63 | — |

By heating the alcoholate in sealed tubes to 110°—115° for four hours, a dark brown liquid is obtained, from which a small number of prismatic crystals belonging to the monoclinic system slowly separate out. Analysis proves these crystals to be antimony trichloride.

The liquid contents of the tubes are brought into a retort fitted with a receiver which is surrounded by a freezing mixture. On gently heating the retort by means of an oil-bath, a copious evolution of hydrochloric acid gas takes place, and a considerable quantity of a colourless mobile liquid collects in the receiver. The distillate shows itself to be ethyl chloride, by its insolubility in water and low boiling point, by burning with a green flame, and by its characteristic odour. The distillation is now carried on in a vacuum, when the temperature of the oil-bath reaches 130° a small quantity of a pale yellow oily liquid comes over; at 160° antimony trichloride distils over and solidifies in the receiver to a semi-transparent crystalline mass. The small quantity of residue left in the retort consists of antimony trioxide mixed with trichloride and a little organic matter.

### 2. *Antimony Pentachloride Methyl Alcoholate*

resembles the corresponding ethyl-compound in its properties and mode of preparation. The pure substance is deposited from a hot alcoholic solution in leafy or tabular crystals possessing a faint yellow colour. At 81° C. it melts, forming a yellow liquid, which decomposes at 130°, with evolution of hydrochloric acid and methyl chloride

It is a stable body, and may be preserved in well stoppered bottles without undergoing spontaneous alteration.

The results obtained on analysis correspond with the formula $SbCl_5.CH_4O$.

0·2069 gram substance gave 0·3376 gram Ag ..... = 53·55 per cent. Cl
0·2957 gram substance gave 0·6272 gram AgCl + ·0058 Ag ..... = 53·12 per cent. Cl
} mean = 53·33.

0·2069 gram substance gave 0·1238 gram $Sb_2S_3$ of which ·0742 = ·0648 dried in $CO_2$ ..... = 37·18 Sb.

0·6625 gram substance gave 0·3979 gram $Sb_2S_3$ of which 0·361 = 0·3118 dried in $CO_2$ ..... = 37·24 „

0·5407 gram substance gave 0·3265 gram $Sb_2S_3$ of which 0·301 = 0·2543 dried in $CO_2$ ..... = 36·60 „

Mean of Sb determinations 37·01

0·3765 gram substance gave 0·0497 gram $CO_2$ and 0·044 gram $H_2O$ = 3·6 per cent. $CO_2$, and 1·29 p. c. $H_2O$.

| | Calculated for $SbCl_5CH_4O$. | Found. |
|---|---|---|
| Sb ..... | 36·80 | 37·01 |
| Cl ..... | 53·55 | 53·33 |
| O ..... | 4·82 | — |
| C ..... | 3·62 | 3·60 |
| H ..... | 1·20 | 1·29 |

The corresponding compound of amyl alcohol has not been obtained in a state of sufficient purity to admit of analysis. It is less stable than the ethyl and methyl compounds, and its preparation is attended with difficulties, as the action of amyl alcohol even on frozen antimony pentachloride is very violent.

This substance forms white starlike crystals, often discoloured by decomposed alcohol.

### 3. *Compound of Ether and Antimony Pentachloride.*

By the action of ether on titanium tetrachloride, Bedson (*Journal Chem. Soc.*, 1876, i, 311) has obtained a crystalline body consisting of one molecule of ether united to one of titanium tetrachloride, $T_iCl_4.C_4H_{10}O$.

Antimony pentachloride forms a similar molecular compound. It is best prepared by cautiously mixing together ether and the pentachloride in the proportion of their molecular weights. The mixture must be well cooled, for should the temperature rise to 70°, decomposition at once takes place.

The freshly prepared substance exists in the form of a finely divided crystalline powder of a greyish-white colour. It is soluble in ether and alcohol, but is decomposed by water. It is very hygroscopic. The crystals melt at 68°—69°; they are very unstable, even at the ordinary temperature they blacken spontaneously; if heated up to their melting point for a few minutes, decomposition takes place.

Analysis gave the following results:—

| | | |
|---|---|---|
| 0·4912 gram substance gave | 0·9287 AgCl + 0·0108 Ag | = 47·49 Cl |
| | 0·2685 gram $Sb_2S_3$ of which 0·1915 = 0·16 $Sb_2S_3$ dried in $CO_2$ ..... | = 32·77 Sb |
| 0·3298 gram substance gave | 0·173 gram $Sb_2S_3$ of which 0·1065 = 0·0921 $Sb_2S_3$ dried in $CO_2$ ..... | = 32·56 Sb |
| | 0·6124 AgCl + 0·0111 Ag..... | = 47·05 Cl |
| 0·3298 gram substance gave | 0·6203 „ + 0·008 „ ..... | = 47·32 Cl |
| | 0·1741 $Sb_2S_3$ of which 0·1401 = 0·1221 dried in $CO_2$..... | = 33·01 |

Mean of Cl determinations 47·29; mean of Sb determinations 32·78 per cent.

| | Calculated for $SbCl_5C_4H_{10}O$. | Found. |
|---|---|---|
| Sb ..... | 32·66 | 32·78 |
| Cl ..... | 47·52 | 47·29 |
| C ..... | 12·85 | — |
| H ..... | 2·68 | — |
| O ..... | 4·29 | — |

## XX.—*On a New and Convenient Form of Ureometer for Clinical Use.*

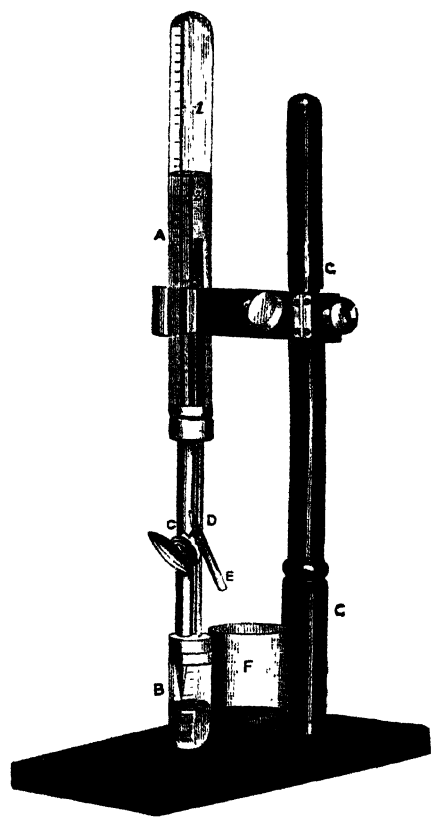
By J. Galley Blackley, M.B., Lond.

Having lately had occasion to make a considerable number of quantitative determinations of the urea contained in urine, I have been much struck with the want of a simple form of apparatus which should give results sufficiently accurate to be of real service in any prolonged series of observations.

The more exact methods for the determination of urea in organic

liquids are far too complex and tedious to be of more than occasional service to the busy medical man, whilst the readier methods are not sufficiently accurate to be of more than approximate value. The method of estimating urea by means of a solution of hypobromite of soda, given by Hüfner (*Journ. f. prakt. Chemie* [2], iii, 1), and the modification of it proposed by Messrs. Russell and West, are on the whole the most convenient for clinical purposes, but even these leave something to be desired on the score of accuracy.

With the view of simplifying the operation of ureometry to the utmost extent compatible with the necessary degree of accuracy, I have devised the simple form of apparatus represented in the accompanying wood-cut, which is in fact a modification of Russell and West's ureometer. It consists of two graduated tubes, a larger one, A, of about 75 c.c. capacity, and a smaller one, B, of about 15 c.c. capacity, closed by perforated india-rubber stoppers, through which pass the tubes C and D. C is the wider of the two, and is provided with a glass stop-cock; its lower extremity drawn to a fine point descends about half way into the tube B; D is a narrower tube, and ascends about half way inside A. E is a short, slightly bent tube, passing through the india-rubber stopper into the tube A, and serving as an egress for the superfluous contents of A, which are collected in the beaker F, the whole being supported by the wooden stand G G.




The method of using the apparatus is as follows:—

Five cubic centimeters of the liquid to be examined are placed in the tube B, and the cork inserted to the level of a scratch on the outside of the tube, the stop-cock being turned off. The tube A is now filled with a solution of hypobromite of soda, and its stopper inserted.

The apparatus is then placed in position on the stand, and the stop-cock gradually opened. The hypobromite solution flows down the tube C, decomposition takes place, and the gases evolved ascending through the tube D, are collected in A. The superfluous hypobromite solution flows out through the tube E into the beaker F. To complete the operation the apparatus is removed from the stand, after placing the finger over the mouth of the tube E, and agitated for a few moments. It is then replaced, and after allowing time for the froth to subside the quantity of gas collected is read off. After subtracting the small constant of air contained in the tube B, the remainder gives by calculation the quantity of urea present in the 5 c.c. of liquid examined. Under ordinary circumstances the whole operation may be completed in five or six minutes.

Instead of having the tube A graduated in cubic centimeters, I have found it convenient to use the tube supplied with Messrs. Russell and West's ureometer, which is graduated so as to show at once without calculation the percentage of urea contained in the liquid under examination.

The following numbers obtained, after taking solutions of urea of known strengths, will serve to give an idea of the degree of accuracy obtainable with the apparatus. The solutions employed contained 10 and 20 grams per litre respectively, 5 c.c. being taken in each experiment. The numbers in the third column are obtained from those in the second by multiplying by $\frac{100}{92}$, and the pretty close agreement between the numbers thus found and the quantities actually taken, quite bears out the statement of Messrs. Russell and West that there is a deficiency of about 8 per cent. in the amount of nitrogen given off when hypobromite of sodium acts upon urea.

| | Experiment 1. | Experiment 2. | Experiment 3. |
|---|---|---|---|
| Weight taken .. | 0·0500 gram | 0·1000 gram | 0·1000 gram |
| Weight of urea calculated from actual vol. of N obtained ..... | 0·04756 „ | 0·9384 „ | 0·9062 „ |
| Corrected weight of urea found .. | 0·0517 „ | 0·1020 „ | 0·985 „ |
| Ratio of weight taken to corrected weight found ..... | 1 to 1·034 „ | 1 to 1·020 „ | 1 to 0·985 „ |

The apparatus is in the hands of Messrs. E. Cetti and Co., of Brooke Street, Holborn, and may be obtained from them.

## XXI.—*Note on the Perbromates.*

By M. M. Pattison Muir, F.R.S.E., Assistant Lecturer on Chemistry, the Owens College.

In a short paper read to the Society in 1874 (*Chem. Soc. J.* [2], xii, 324), I stated that perbromic acid could be readily prepared by the action of bromine upon the hydrate of perchloric acid dissolved in water. This reaction, which is originally due to Kämmerer, has been called in question by MacIvor (*Chem. News*, xxxii, 35).

Since the date of my note in 1874 I have repeatedly attempted to prepare further quantities of perbromic acid, with the view of studying its salts, but invariably without success.

Kämmerer says that he has found great difficulty in preparing the acid by means of the above-cited reaction. He recommends that silver carbonate be added after the action has continued for some time, and states that silver perbromate may then be obtained.

I have repeated this experiment of Kämmerer. A quantity of aqueous perchloric acid, previously heated for some time in an open vessel, in order to remove any of the lower acids of chlorine (which according to Kämmerer retard the formation of perbromic acid), was mixed with an excess of bromine and gently warmed for some hours in a flask fitted with an inverted receiver. Freshly prepared silver carbonate was then added, and the heating was continued for a short time. On examining the liquid, it was found to contain perchlorate and bromide of silver, but no perbromate.

I must therefore correct my former statement that "perbromic acid can be easily obtained by the action of bromine upon the hydrate of perchloric acid dissolved in water." The conditions under which this reaction becomes possible are as yet ill-defined, if not altogether unknown. Probably the tension of the bromine or chlorine vapour plays an important part; but as a means of preparing the wished for acid, the reaction must, I think, be abandoned.

I have also attempted to prepare perbromic acid by the electrolysis of bromic acid, but without success. Bromine and oxygen were evolved, but without the formation of a higher oxy-acid.

The relations of the halogens and of their compounds to one another are most interesting. These reactions serve at any rate to give us negative information.

I hope at some future time to return to the study of the mutual relations existing between the oxy-acids of chlorine, bromine, and iodine.

# ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

## General and Physical Chemistry.

**Theory of Spectra; Observations on the Last Communication of J. N. Lockyer.** By LECOQ DE BOISBAUDRAN (Compt. rend., lxxxii, 1264—1266).

LOCKYER has brought forward the hypothesis that, at a high temperature, the elementary molecule is broken up, either into sub-molecules of the same element, or into those of distinct elements; also that every element decomposes into as many simpler substances as there are rays in its spectrum. The variation in the relative intensities of rays by change of temperature, is explained in a similar manner, and it is upon this latter ground that the elementary nature of calcium is questioned by Lockyer, since its two rays H, and $H_2$, change in relative brilliancy according to the heat at which it is volatilised.

The author admits the probability of a molecular condensation in the cases of sulphur and iodine, but thinks that the arguments advanced in the case of calcium are not sufficiently well supported. According to his own observations, the relative intensity of the spectral rays of all the elements changes with a variation of temperature, and he thinks that if, in the face of the immense number of rays known to exist in the spectra of some elements, the former theory is to be admitted in preference to that of harmonic vibrations, it ought to be supported by well-established facts very different from those actually known. Stokes has suggested that "probably with an increase of temperature, the more refrangible lines become brighter at the expense of the less refrangible." Whether this be really the case or not, it is quite certain that with many substances, the less refrangible rays do undergo a very great diminution in brilliancy, at the time that the more refrangible rays increase in brilliancy. This fact the author pointed out in a memoir published in the *Compt. rend.* for 1871, relative to certain experiments on the action of the induction spark on solutions of stannic chloride.

While admitting that Lockyer's hypothesis is exceedingly plausible, and moreover supported by the well known close relations which exist between the properties of simple and compound bodies belonging to the same family, he thinks that at present no experimental result has been obtained which will warrant a philosophical belief in the multiple nature of the so-called elementary bodies.

J. W.

**Remarks on the Actual Existence of Matter formed of Isolated Atoms Comparable with Material Points.** By M. BERTHELOT (Compt. rend., lxxxii, 1226—1231).

THE experiments of Kundt and Warburg on the velocity of sound in mercurial vapour have led them to conclude that the molecule of mercurial gas behaves, as far as its mechanical and thermic properties are concerned, sensibly as a material point. They make use of the formula of Clausius, $\frac{K}{H} = \frac{3}{2}\frac{\gamma' - \gamma}{\gamma}$. Where K represents the *vis viva* or working force of the movement of translation; H, the total *vis viva*; $\gamma$ and $\gamma'$, the specific heats taken at constant volume and constant pressure.

The author is of opinion that formulæ containing specific heats deduced from the theory of perfect gases are inapplicable to the vapour of mercury, since such formulæ imply that the specific heats are independent of temperature. Now, experience has shown that with the majority of gases the specific heat at constant pressure varies with the temperature, even to the extent of one-fourth or one-half; it is also very probable that the specific heat at constant volume varies in a similar manner, so that the relation $\gamma' - \gamma$ between the specific heats, upon which the whole discussion turns, would always be a variable quantity.

If we admit with Clausius that the difference $\gamma' - \gamma$ is constant for all gases, representing the heat consumed by the exterior work of dilatation, nevertheless since $\gamma$ diminishes rapidly with the temperature, the relation $\frac{\gamma' - \gamma}{\gamma}$ will go on increasing as the temperature falls, while the denominator diminishes without ceasing; numbers would therefore be obtained much higher than the supposed constant 1·41.

A gas formed of material points or of atoms incapable of intramolecular movement, would in all probability exhibit very exceptional properties; thus it should not furnish lines by spectral analysis, since the formation of such lines appears to depend especially upon intramolecular vibrations. Again, the liquid and solid resulting from the condensation of such a gas (mercurial vapour) would probably possess properties very different from the products of condensation of other gases, such as hydrogen, gaseous iodine, or volatilised potassium.

The author also brings forward a few other arguments, in which he shows that with respect to cohesion and facility of crystallisation, solid mercury does not differ materially from solid potassium; he thinks that no satisfactory conclusion can be drawn from the fact that mercurial vapour forms an exception to Avogadro's law, since it is very easy to imagine that the atom may be formed by an aggregation of a multitude of smaller particles, without doing violence to any of our well-established chemical theories. The notion supported by some chemists, that there exists but one fundamental substance, whose multiple and varied states of aggregation constitute the simple bodies with which we are acquainted, with all their specific properties, seems

to imply that the atomic masses of those elements which, like mercury, have high atomic weights, are very far removed from the state of veritable atoms.

J. W.

**Atomic Constitution of Bodies.** By M. DE SAINT-VENANT (Compt. rend., lxxxii, 1223—1226).

BERTHELOT has stated that "the very idea of an atom, indivisible, and yet possessing extension and continuity, as well as that of an atom gifted with mass and yet reduced to a material point, seems contradictory in itself." Respecting the latter portion of this statement, the author remarks that in his opinion, there is nothing contradictory in supposing that an atom without extension can move with varying rapidity, under the influence of attractive and repulsive forces, emanating from other atoms equally without dimensions; that it is not absurd to suppose that, in its turn, an atom should exert an equal and contrary force upon an adjacent atom, with an intensity varying according to the distance, so that at every instant there would be communicated to each pair of atoms, components of acceleration, either equal for both or constantly greater for one than for the other; in a word, that it is reasonable to endow material points with mobility, mass, inertia, and action; or with properties similar to those which have been attributed to the grosser atoms of the old philosophers. He thinks that there is not necessarily any logical bond between the idea of existence, even material, and the idea of extension. A body without extent would still be a corporeal element, if, obeying unconsciously dynamical laws, it occupied at each instant a determinate position in space, whether such position be regarded as absolute, or merely relative to that of other elements, equally consisting of material points; that is to say, if in its excursions it is transported from one position to another, with its essential properties unaltered, and therefore retaining specially that property whereby it is recognised by the senses.

From considerations founded upon a study of the laws of continuity, Boscowich evolved the notion of the material atom destitute of extension, an idea which was further developed by Bernouilli, Leibnitz, Wolf and Kant; many recent authors, however, desiring to extend to elastic, spongy, or semi-solid substances, the formulæ of elasticity of solids, and having been thereby compelled to increase the number of coefficients, and to render them independent of each other, at last proceeded to condemn, under the name of the "theory of Boscowich," not only his capital idea of the reduction of atoms to centres of dynamic action, but even the general physical law of the reciprocal action of particles upon each other as functions of the distance between them. The author contends against this summary rejection of the views of Boscowich, pointing out that it amounts to a condemnation of the teaching of Laplace, if not to the actual setting aside of the Newtonian theory itself.

He concludes with Berthelot that it is impossible, without arguing in contradiction to the experience obtained in the observation of terrestrial and celestial phenomena, to regard atoms as corpuscles formed of hard

continuous matter, but he thinks that there is nothing contradictory in regarding them as material points possessing all the properties, minus extension, which are common to visible and tangible bodies.

J. W.

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## Thermic Researches on Hyposulphurous Acid.

By M. BERTHELOT (Compt. rend., lxxxiii, 416—418).

WITH the view of investigating the thermic conditions of the formation of this acid, the author has measured the heat disengaged when oxygen is absorbed by a solution of sodium-zinc hyposulphite $(SO_2)_2 ZnNa_2$. About 650 c.c. were taken of a solution capable of absorbing six times its volume of oxygen, contained in a flask serving as a calorimeter, as in the experiments already published on chlorine and hypochlorites. Pure oxygen was passed into it, and the weight absorbed ascertained at various stages, up to the absorption of a weight equal to about the half of the quantity necessary to saturate the liquid. The heat disengaged at the moment of absorption does not exceed the half or the third of the total quantity. The remainder is developed during the ten or eleven following minutes, as if two successive compounds were produced. Three trials were made with the same solution (capable of absorbing 4·40 grams oxygen), and the following numbers obtained :—

| | Oxygen absorbed. Grams. | Heat disengaged referred to 16 grams of oxygen. kilo.-degrees. |
|---|---|---|
| 1st portion..... | 0·753 | 34·00 |
| 2nd portion ..... | 0·769 | 34·01 |
| 3rd portion ..... | 0·859 | 33·82 |
| | 2·381 | 33·94 |

These numbers represent the transformation of the hyposulphites of sodium and zinc into the corresponding sulphites. To pass to hyposulphurous acid, we must know the difference between the heats of neutralization of hyposulphurous and sulphurous acids by soda and zinc oxide. These quantities are unknown, but they may be taken as comprised between 0 and 3 heat-units. The heat of transformation of hyposulphurous acid in solution into dilute sulphurous acid, viz. :—

$$SO_2H_2 \text{ dissolved} + O \text{ gas} = SO_2 \text{ dissolved},$$

is therefore equal to $34 - \alpha$ where $\alpha$ is comprised between 0 and 3.

This quantity of heat is nearly the same as the heat disengaged by the analogous transformation of sulphurous acid into dilute sulphuric acid :—

$$SO_2 \text{ dissolved} + O \text{ gas} = SO_4H_2 \text{ dilute} : + 32{\cdot}15.$$

There is here, therefore, an approximate proportionality between the quantities of heat disengaged and the proportions of oxygen fixed, as observed by Dulong in more than one instance.

This proportionality does not extend beyond the first term of the series of the oxygen-compounds of sulphur.

$S + O + \text{water} = SO_2H_2$ dilute disengages $8{\cdot}7 - \alpha$, that is, the

fourth of the preceding quantity, admitting that $S + O_2 = SO_2$ gas disengages 38·8 heat-units, the mean of the values obtained by Dulong, Hess, Andrews, and Favre and Silbermann.

Neglecting $\alpha$ for simplicity, we have :—

$$\left.\begin{array}{lll} S + O + H_2O & = SO_2H_2 \text{ dilute} \ldots\ldots & + 8{\cdot}7 \\ S + O_2 + H_2O & = SO_3H_2 \text{ dissolved} \ldots & + 42{\cdot}6 \\ S + O_3 + H_2O & = SO_4H_2 \text{ dilute} \ldots\ldots & + 74{\cdot}7 \end{array}\right\} \begin{array}{l} 34 \\ 32 \end{array}$$

Further:

$$\begin{array}{lll} S + H_2 + O_2 + \text{water} & = SO_2H_2 \text{ dilute} \ldots\ldots & + 43{\cdot}2 \\ S + H_2O_2 & = SO_2H_2 \text{ dilute} \ldots\ldots & + 19{\cdot}5 \\ SO_2 + H_2 + \text{water} & = SO_2H_2 \text{ dilute} \ldots\ldots & + 0{\cdot}6 \\ H_2S \text{ solution} + O_2 & = SO_2H_2 \text{ dilute} \ldots\ldots & + 38{\cdot}6 \end{array}$$

The decomposition of hyposulphurous acid into sulphuric acid and hydrogen sulphide in solution would disengage—

$$2SH_2O_2 \text{ dilute} = SH_2O_4 \text{ dilute} + H_2S \text{ dissolved} = + 27{\cdot}4.$$

In the change of hyposulphurous acid into thiosulphuric acid (admitting Thomsen's values for the latter)—

$$2SO_2H_2 \text{ dilute} = S_2O_3H_2 \text{ dilute sets free} + 20{\cdot}6,$$

a quantity which explains the greater stability of ordinary thiosulphates, "*Molecular systems being, under given circumstances, so much the more stable in proportion as they have lost a greater amount of their energy.*

H. W.

## On the Amount of Heat evolved in the Formation of the Two Isomeric Propylic Aldehydes. By M. Berthelot (Compt. rend., lxxxiii, 413—415).

The specimen of normal propylic aldehyde with which the research was made, had a boiling-point of 47°—47·5°.

The heat of formation of a normal aldehyde can be exactly determined by the heat disengaged in its change into the corresponding acid, as shown in the author's researches on ethylic aldehyde (*Compt. rend.*, Jan., 1876). The same method was followed in this research, excepting that the action of the potassium permanganate was stopped after four or five minutes, so as to prevent a further oxidation. Under these conditions, the change takes place as indicated by theory, 58 grams of normal propylic aldehyde absorbing 16·12 grams and 16·85 grams of oxygen in the calorimetric trials, that is O for $C_3H_6O$ :—

$C_3H_6O$ dissolved + O gas = $C_3H_6O_2$ dissolved at 23° disengages 69·8 and 70·75, mean 70·3.

$C_3H_6O$ pure + 840 $H_2O$ at 23° disengages + 4·6.

Admitting that $C_3H_6O_2$ liquid + water disengages + 0·5, we find—

$$C_3H_6O \text{ pure} + O = C_3H_6O_2 \text{ pure, gives off} + 74{\cdot}2,$$

a number nearly identical with 70·1, developed by the transformation of ethylic aldehyde into acetic acid.

The same numbers, very nearly, are applicable to the change of a gaseous aldehyde into a gaseous acid. They exceed by nearly one-fourth the heat of combustion of hydrogen:—

$$H_2 + O = H_2O \text{ gas} : + 59.$$

*Heat of Combustion.*—Admitting that the heat of combustion of 1 gram of propionic acid is 4·690 heat-units, according to Favre and Silbermann, the author finds for that of $C_3H_6O_2 = 74$ grams, the value 345·6 heat units. From which it follows that the heat of combustion of normal propylic aldehyde, $C_3H_6O = 58$ grams is 419·6, or more simply 420 heat-units.

*Formation from the Elements.*—

$$C_3 \text{ (diamond)} + H_6 \text{ gas} + O = C_3H_6O \text{ liquid, gives off} + 69 \text{ h.-units.}$$

From normal propylic alcohol:—

$$C_3H_8O + O = C_3H_6O + H_2O \text{ liquid, gives off} + 56 \text{ heat-units.}$$

From propylene:—

$$C_3H_6 \text{ gas} + O = C_3H_6O \text{ liquid} + 72{\cdot}5 \text{ gas} + 66 \text{ nearly,}$$

numbers which are not far from the heat of formation of water from hydrogen.

The formation of normal propylic aldehyde seems, moreover, to be really effected when propylene is treated with chromic acid, a reaction which disengages about 6 heat-units more. Only normal propylic aldehyde partly changes into propionic acid under these conditions. This reaction is simultaneous with the formation of isopropylic aldehyde (acetone), at the expense of another portion of propylene; a formation which disengages a quantity of heat nearly the same, say 68·5 instead of 72·5.

The similarity between the heats of formation of normal propylic aldehyde and of acetone by means of propylene, is found again between the heats of combustion and the heats of formation of the two aldehydes. In fact, the heat of combustion of acetone, found by experiment, is 424 heat-units, instead of 420. The heat given off by the union of the elements of acetone is 65 instead of 69.

It follows from these data that the *transformation of a normal primary aldehyde into a secondary isomeric aldehyde sets free little or no heat.*

Numbers, independent of the preceding, for the two propylic alcohols lead to the same conclusion. Hence it follows that the transformation of each of the alcohols into the corresponding aldehyde sets free nearly the same quantity of heat; a result agreeing likewise with that which experience has shown for the transformation of these two alcohols into the corresponding propylsulphuric acids; also for the formation of the acid chlorides and bromides of the three isomeric valeric acids, and of the two butyric acids, as well as the dissolved salts.

These various acids have also been shown to disengage nearly the same quantities of heat in their formation. It is the same for the thermic formation of the dissolved ethylsulphates and isethionates. If we add that the two isomeric acids, ethylsulphuric and isethionic,

are formed from alcohol and sulphuric acid, with disengagement of amounts of heat nearly identical, we are led, by the similarity of the results obtained on such different bodies, to the important general conclusion, that "*isomeric bodies of similar chemical function are formed, from their elements, with disengagements of almost identical amounts of heat, and this identity of heat-development is likewise observed in the formation of their isomeric derivatives.*

We may account for this law by observing that the difference between the particular arrangements of such bodies is too small to admit any great difference between the amounts of molecular work accomplished in their formation. It must, however, be remembered that the same law does not hold good when a substance is changed into a polymeride, which is equivalent to a real chemical combination, and produces in most cases, a disengagement of heat. There is also a disengagement of heat, if a body is changed into an isomeride more stable, denser, less volatile, and having a different chemical function,—acetic ether, for example, into butyric acid.

H. W.

## Inorganic Chemistry.

**Action of Hydrogen Chloride and Hydrogen Bromide on Selenious Anhydride.** By A DITTE (Compt. rend., lxxxiii, 56—58).

*Hydrogen Chloride.*—Selenious anhydride absorbs dry hydrogen chloride rapidly with considerable rise of temperature. The product first formed is an amber-yellow liquid composed of equal numbers of molecules of the two constituents ($SeO_2HCl$). This liquid, when heated, begins to give off hydrogen chloride at 26°. Its dissociation-tension in millimeters at various temperatures is as follows:—

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Temperature .. | 30° | 40° | 55° | 75° | 100° | 106° | 118° |
| Tension ..... | 15 | 48 | 142 | 313 | 664 | 760 | 1012 |

At low temperatures the liquid continues to absorb hydrogen chloride, and ultimately becomes converted into a transparent yellow crystalline solid, containing two molecules of hydrogen chloride to one of selenious anhydride ($SeO_2 2HCl$). This substance is resolved by heat (its dissociation-tension being considerable even at the ordinary temperature) into hydrogen chloride and the compound $SeO_2HCl$, which latter is permanent below 26°. The following tensions in millimeters were observed:—

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Temperature .. | −20° | 0° | 12° | 15° | 22·5° | 30° | 33° |
| Tension ..... | 60 | 219 | 418 | 483 | 672 | 760 | 993 |

*Hydrogen Bromide.*—Selenious anhydride absorbs dry hydrogen bromide energetically, forming in the first place the compound

$SeO_2 2HBr$, which crystallises in brilliant steel-grey spangles. This compound is stable below 55°, but at higher temperatures it is decomposed into selenium, bromine, and water. Its solution in a very small quantity of water is nearly black: more water resolves it into hydrobromic and selenious acids.

J. R.

## Production of Carbon Monosulphide. By S. Kern (Chem. News, xxxiii, 253).

Iron wire digested for six weeks in carbon disulphide completely reduced it to iron disulphide and carbon monosulphide, which latter was left as a reddish-brown powder upon dissolving the iron disulphide in hydrochloric acid.

F. J. L.

## On the Strength of Ammonia Solution. By O. Wachsmuth (Arch. Pharm. [3], vi, 510—514).

Water was saturated with ammonia at 0°, and it was found that it had increased in volume from 100 c.c. to 203 c.c., had a sp. gr. of 0·866, and when neutralised with hydrochloric acid yielded 149·7 per cent. of dry ammonium chloride. The amount of ammonia, therefore, present by weight was 47·55 per cent., so that 1 gram of water contained 0·906 gram = 1193 c.c. ammonia. When heated to 10°, its sp. gr. rose to 0·87; and when allowed to evaporate spontaneously at 15°—25° it lost 49 per cent. of its volume, 1·35 per cent. of ammonium carbonate being formed. The concentrated solution was then diluted, the sp. gr. being determined at each addition, and the amount of ammonia present determined by hydrochloric acid. The author finds that for the better working of Carré's ice-machine, concentrated ammonia solution is necessary. The following table of the amount of ammonia contained in solutions of various sp. grs. is given:—

| Specific gravity at 12° C. | 1 kilo. contains ammonia in grams. | 1 litre contains ammonia in grams. | 1 litre consists of: | |
|---|---|---|---|---|
| | | | Water in c.c. | Liquid ammonia in c.c. |
| 0,870 | 384,4 | 334,5 | 535,5 | 464,5 |
| 0,872 | 376,9 | 328,6 | 543,4 | 456,6 |
| 0,874 | 369,4 | 322,8 | 551,2 | 448,8 |
| 0,876 | 362,0 | 317,1 | 558,9 | 441,1 |
| 0,878 | 354,6 | 311,3 | 566,7 | 433,3 |
| 0,880 | 347,2 | 305,5 | 574,5 | 425,5 |
| 0,882 | 340,0 | 299,8 | 582,2 | 417,8 |
| 0,884 | 332,9 | 294,2 | 589,8 | 410,2 |
| 0,886 | 325,8 | 288,6 | 597,4 | 402,6 |
| 0,888 | 318,7 | 283,0 | 605,0 | 395,0 |
| 0,890 | 311,6 | 277,3 | 612,7 | 387,3 |
| 0,892 | 304,7 | 271,7 | 620,3 | 379,7 |

| Specific gravity at 12° C. | 1 kilo. contains ammonia in grams. | 1 litre contains ammonia in grams. | 1 litre consists of: | |
|---|---|---|---|---|
| | | | water in c.c. | Liquid ammonia in c.c. |
| 0,894 | 297,8 | 266,2 | 627,8 | 372,2 |
| 0,896 | 290,9 | 260,6 | 635,4 | 364,6 |
| 0,898 | 284,1 | 255,1 | 642,9 | 357,1 |
| 0,900 | 277,3 | 249,5 | 650,5 | 349,5 |
| 0,902 | 270,7 | 244,1 | 657,9 | 342,1 |
| 0,904 | 264,1 | 238,7 | 665,3 | 334,7 |
| 0,906 | 257,7 | 233,4 | 672,6 | 327,4 |
| 0,908 | 251,3 | 228,2 | 679,8 | 320,2 |
| 0,910 | 244,9 | 222,8 | 687,2 | 312,8 |
| 0,912 | 238,6 | 217,6 | 694,4 | 305,6 |
| 0,914 | 232,3 | 212,3 | 701,7 | 298,3 |
| 0,916 | 226,0 | 207,0 | 709,0 | 291,0 |
| 0,918 | 219,7 | 201,6 | 716,4 | 283,6 |
| 0,920 | 213,4 | 196,3 | 723,7 | 276,3 |
| 0,922 | 207,3 | 191,1 | 730,9 | 269,1 |
| 0,924 | 201,2 | 185,9 | 738,1 | 261,9 |
| 0,926 | 195,1 | 180,6 | 745,4 | 254,6 |
| 0,928 | 189,0 | 175,4 | 752,6 | 247,4 |
| 0,930 | 182,9 | 170,1 | 759,9 | 240,1 |
| 0,932 | 176,9 | 164,8 | 767,2 | 232,8 |
| 0,934 | 170,9 | 159,6 | 774,4 | 225,6 |
| 0,936 | 164,9 | 154,3 | 781,7 | 218,3 |
| 0,938 | 158,9 | 149,0 | 789,0 | 211,0 |
| 0,940 | 152,9 | 143,7 | 796,3 | 203,7 |
| 0,942 | 147,1 | 138,5 | 803,5 | 196,5 |
| 0,944 | 141,3 | 133,3 | 810,7 | 189,3 |
| 0,946 | 135,6 | 128,2 | 817,8 | 182,2 |
| 0,948 | 129,9 | 123,1 | 824,9 | 175,1 |
| 0,950 | 124,2 | 118,0 | 832,0 | 168,0 |
| 0,952 | 118,7 | 113,0 | 839,0 | 161,0 |
| 0,954 | 113,2 | 108,0 | 846,0 | 154,0 |
| 0,956 | 107,8 | 103,0 | 853,0 | 147,0 |
| 0,958 | 102,4 | 98,1 | 859,9 | 140,1 |
| 0,960 | 97,0 | 93,1 | 866,9 | 133,1 |
| 0,962 | 91,6 | 88,1 | 873,9 | 126,1 |
| 0,964 | 86,2 | 83,0 | 881,0 | 119,0 |
| 0,966 | 80,8 | 78,0 | 888,0 | 112,0 |
| 0,968 | 75,5 | 73,0 | 895,0 | 105,0 |
| 0,970 | 70,2 | 68,0 | 902,0 | 98,0 |
| 0,972 | 65,2 | 63,3 | 908,7 | 91,3 |
| 0,974 | 60,2 | 58,6 | 915,4 | 84,6 |
| 0,976 | 55,2 | 53,8 | 922,2 | 77,8 |
| 0,978 | 50,2 | 49,1 | 928,9 | 71,1 |
| 0,980 | 45,3 | 44,3 | 935,7 | 64,3 |
| 0,982 | 40,4 | 39,6 | 942,4 | 57,6 |
| 0,984 | 35,5 | 34,9 | 949,1 | 50,9 |
| 0,986 | 30,6 | 30,1 | 955,9 | 44,1 |
| 0,988 | 25,8 | 25,5 | 962,5 | 37,5 |
| 0,990 | 21,0 | 20,7 | 969,3 | 30,7 |

E. W. P.

**Reducing Action of Phosphine.** By W. R. H. (Chem. News, xxxiv, 14).

If the reducing action of phosphine on sulphuric acid be carried to excess, reduction to sulphurous anhydride takes place, with separation of sulphur.

F. J. L.

**On the Action of Magnesium on some Metallic Salts.** By S. Kern (Chem. News, xxxiii, 236).

The reactions in aqueous solutions are as follows, hydrogen being evolved in every case:—

Manganous chloride produces manganous oxide, which rapidly oxidises to trimanganic tetroxide. Uranic nitrate yields uranic oxide. Potassic dichromate forms potassic hydroxide. Aluminium salts produce aluminic hydrate. Palladium salts yield the monoxide, also hydrogenated metal. Copper salts give a precipitate of copper; ammonium salts yield ammonia and nitrogen.

F. J. L.

**Decomposition of Insoluble Carbonates by Hydrogen Sulphide.** By L. Naudin and F. de Montholon (Compt. rend., lxxxiii, 58—60).

When barium carbonate suspended in water at 10° is treated with a slow current of hydrogen sulphide, it is gradually converted into barium sulphide, the conversion being partial or complete according to the proportion of water present. Thus, of 100 parts of the carbonate suspended in 10 times its weight of water, 15·3 parts were converted into sulphide in five hours; of the same quantity of carbonate suspended in 50 times its weight of water, 51·2 parts were converted into sulphide in six hours; whilst carbonate suspended in 100 times its weight of water was completely converted into sulphide in 30 hours. The solution of barium sulphide formed was colourless at first, but turned yellow in the air.

Magnesium, zinc, and lithium carbonates behaved in the same manner as barium carbonate.

J. R.

**Mercuric Iodate: its Preparation and Reactions.** By C. A. Cameron (Chem. News, xxxiii, 253).

This salt is precipitated when alkaline iodates or iodic acid are added to mercuric acetate or nitrate, but not when added to the chloride. It is soluble in alkaline chlorides, bromides, iodides, cyanides, and cyanates; in dilute solutions of manganese and zinc chlorides; in disodic hyposulphite and in hydrochloric acid. It is insoluble in solutions of potash, soda, ammonia, sodium sulphite, borax, corrosive sublimate, hydro-disodic phosphate, alkaline iodates, chlorates and bromates, and in acetic, fluoric, and silicofluoric acids.

If dissolved in a salt of the alkalis and evaporated, an iodate of the alkali first crystallises out, and then double salts of mercury.

F. J. L.

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## On the Sulphides of Arsenic and their Compounds.

By L. F. NILSON (J. pr. Chem. [2], xiii, 1—61).

I. *Arsenic Trisulphide.*—When arsenic trisulphide is added to a concentrated boiling solution of sodium or potassium carbonate, arsenic disulphide is precipitated. After removal of the disulphide the solution was allowed to cool, and a bulky brown precipitate subsided, which was decomposed by water. After separation by filtration through cloth, and treatment with boiling hydrochloric acid, a pure yellow residue remained. The brown compound on analysis was found to have the formula $NaAs_3S_5 + 4H_2O$(or $Na_2.3As_2S_3 + 8H_2O$).

When, instead of allowing the solution of arsenic trisulphide in sodium carbonate to cool, it was kept for a long time at 70°—80°, a yellowish-brown crust deposited. This substance is soluble in alkalis and in ammonia. It consists of slightly impure arsenic trisulphide. When the above-mentioned solution, after removal of arsenic disulphide, is evaporated till it solidifies on cooling, an amorphous brown mass is obtained, which on standing deposits four different crystalline substances. The first of these consists of garnet-red hexagonal crystals (sometimes short prisms), which are sparingly soluble in water. It was purified by washing with water. After some time, it turned yellow on the surface. It is soluble in alkaline liquids, and when treated with hydrochloric acid, decomposes, leaving a yellow residue. On analysis, numbers were obtained which agreed best with the formula $Na_2As_4S_6O_5 + 7H_2O$(or $Na_2O.2As_2S_3O_2 + 7H_2O$). The second substance crystallised in well formed yellow monoclinic prisms, which easily dissolved in water. Hydrochloric acid added to its solution threw down a yellow flocculent precipitate of sulpharsenic acid. The crystals were found to consist of sodium sulpharsenate, $2Na_3AsS_4 + 15H_2O$.(or $3Na_2S.As_2S_5 + 15H_2O$). On standing over sulphuric acid, it lost all its water of crystallisation. A third salt crystallised in small white crystals. It was washed with cold water, and then dissolved in hot water, with evolution of gas. It consisted of sodium dicarbonate. A fourth salt crystallised in colourless crystals, which dissolved easily in water. Addition of hydrochloric acid produced no change. It proved to be $HNa_2AsO_4 + 7H_2O$(or $2Na_2O.H_2O.As_2O_5 + 14H_2O$). The following, therefore, are the products of the action of a boiling solution of sodium carbonate on arsenic trisulphide :—Carbonic anhydride, sulphuretted hydrogen, arsenic disulphide, acid sodium sulpharsenite, sodium trisulpharseniate, sodium sulpharseniate, sodium arseniate, and sodium dicarbonate. The following reactions account for the formation of these salts :—

$$6As_2S_3 + Na_2CO_3 + 4H_2O = Na_2As_4S_6O_5 + 4As_2S_2 + 4H_2S + CO_2.$$
$$4Na_2As_2S_4 + 6H_2O = 2NaAs_3S_5 + 2Na_3AsO_3 + 6H_2S.$$

The sodium arsenite is converted into arsenate either by decomposi-

tion of water and evolution of hydrogen, or by the oxidising action of the air.

Arsenic trisulphide boiled with a concentrated solution of potassium carbonate gave a deposit of the disulphide. The solution, evaporated to dryness, formed a yellowish-green amorphous mass, which, after standing for two months, gave a solution containing a large amount of small globular red masses. These were washed with water, which decomposes the compound but very slightly. This substance is scarcely attacked by hydrochloric acid, but dissolves in caustic potash to a yellow liquid, which when boiled gives a blackish-brown deposit. On analysis it was found to have the formula—

$$KAs_3S_5 + H_2O (\text{or } K_2S.3As_2S_3 + 2H_2O).$$

Another portion of the amorphous yellowish-green mass was treated with alcohol, and the alcoholic solution was allowed to stand for some time. The whole of the amorphous mass was changed into small colourless pointed crystals of potassium disulpharsenate, $KAsSO_2 + H_2O$, which was described by Cloëz. The reaction is this—

$$3As_2S_3 + K_2CO_3 + 3H_2O = 2KAsSO_2 + 2As_2S_2 + 3H_2S + CO_2.$$

Potassium dicarbonate was formed at the same time. The remaining products are analogous to those from sodium carbonate.

*Salts of Sulpharsenious Acid.*—These salts are prepared by dissolving arsenic trisulphide in the respective sulphhydrates, taking care to exclude air, to prevent formation of sulpharsenates. A mixture of potassium sulphhydrate and arsenic trisulphide deposits, after a few moments, a bulky brown body; the mother-liquor when evaporated deposits $KAsS_2 + 2\frac{1}{2}H_2O$ as an amorphous bright red salt. The gelatinous blood-red compound which results from treating the former salt has the fomula $K_6As_4S_9 + 8H_2O$. By boiling arsenic trisulphide with potassium sulphhydrate for some days, a reddish-brown crust deposited, while sulphuretted hydrogen was evolved; it consisted of microscopic prisms; its formula is $KAs_3S_5 + H_2O$. The following equation probably explains its formation:—

$$4KAsS_2 + 3H_2O = KAs_3S_5 + K_3AsO_3 + 3H_2S.$$

An excess of potassium sulphhydrate transforms the sulpharsenite into sulpharsenate with deposition of arsenic:

$$5K_3AsS_3 = 3K_3AsS_5 + As_2 + 3K_2S.$$

*Sodium Sulpharsenite*, $NaAsS_2$, is a dirty brown amorphous salt, obtained by evaporating a solution of arsenic trisulphide in sodium carbonate to dryness in a vacuum. When the solution is evaporated by heat, a reddish-brown precipitate is formed, consisting of $Na_2As_4S_7 + 6H_2O$; and on boiling it, trisulpharsenate and sulpharsenate of sodium are formed, as well as a dirty brown amorphous substance, consisting of $NaAsS_2 + 1\frac{1}{2}H_2O$. Arsenic trisulphide, with excess of sodium sulphhydrate, gives sodium sulpharsenate which crystallises with 18 molecules of water. Ammonium sulpharsenite, prepared in a similar manner has the formula $(NH_4)_2As_3S_7 + 4H_2O$, and is a bright red

crystalline substance. The mother-liquor on evaporation deposited a small quantity of a crystalline yellow substance, which was not analysed.

*Barium Sulpharsenite*, $Ba(AsS_2)_2 + 2H_2O$, is a dark reddish-brown shining mass. On boiling with hydrochloric acid, it has partially dissolved. The residue consisted of $BaAs_{12}S_{19}$ (or $BaS.6As_2S_3$), and resists the action of hydrochloric acid.

By adding twice as much barium sulphhydrate to arsenic trisulphide and evaporating the resulting solution in a vacuum, sulphuretted hydrogen is evolved, and a greyish-green substance is precipitated which has the formula $Ba_2As_2S_5 + 5H_2O$. If this substance be allowed to remain in its mother-liquor for some time, it turns indigo-blue and retains the colour even after washing with water, in which it is sparingly soluble. It assumes a coppery lustre under the burnisher. It has the same formula as the former salt. When the mother-liquor of the former salt is boiled, a brownish-red deposit settles, and when this is removed, a precipitate consisting of needle-shaped microscopic crystals comes down, probably having the formula $Ba_5As_4S_{11} + 6H_2O$.(or $3BaS.As_2S_3 + 2BaS.As_2S_3 + 6H_2O$. The mother-liquor of this salt yielded large brilliant yellow monoclinic prisms; its formula is $Ba_5As_4S_{13} + 8H_2O$. (or $2BaS.As_2S_3 + 3BaS.As_2S_5 + 8H_2O$). This salt was also prepared by dissolving arsenic pentasulphide in barium sulphhydrate. A saturated solution of the trisulphide in barium sulphhydrate, to which double its volume of sulphhydrate had been added, was evaporated in a vacuum and deposited a greyish-green body, identical with that already described as having that colour. The filtrate from this substance deposited pale yellow prisms, sparingly soluble in water. Its formula is $Ba_3(AsS_3)_2 + 14H_2O$(or $3BaS.As_2S_3 + 14H_2O$). The mother-liquor of this salt then deposited large brilliant monoclinic prisms, also sparingly soluble in cold water, of the formula $Ba_2As_2S_5 + 15H_2O$.

The *Sulpharsenite of Strontium*, $2SrAs_2S_4 + 5H_2O$, is an orange-yellow mass. The salt $Sr_2As_2S_5 + 15H_2O$ resembles the corresponding barium salt in method of preparation and properties.

*Calcium Sulpharsenite*, $CaAs_2S_4 + 11H_2O$, is deposited as a crystalline cake on evaporating a saturated solution of arsenic trisulphide in calcium sulphhydrate. It turns brown when exposed to air, owing to absorption of water. When treated with cold water, it dissolves partially, leaving an amorphous brown residue of $CaAs_8S_{13} + 10H_2O$(or $CaS.4As_2S_3 + 10H_2O$); and on boiling it with water, more calcium sulphide is removed, leaving $CaAs_{18}S_{28} + 10H_2O$(or $CaS.9As_2S_3 + 10H_2O$). When a solution of one molecule of the trisulphide was dissolved in three molecules of calcium sulphhydrate and the solution evaporated in a vacuum, long white nacreous prisms crystallised out, having the composition $Ca_7As_2S_{10} + 25H_2O$(or $7CaS.As_2S_3 + 25H_2O$).

*Magnesium Sulpharsenite*, $Mg(AsS_2)_2 + 5H_2O$, is a brown brittle mass; $Mg_2As_2S_5 + 8H_2O$ is a yellow crystalline precipitate; they are formed in a manner analogous to that in which the calcium salts were prepared. $Mg_3(As_2S_3)_2 + 9H_2O$ is also a crystalline precipitate.

Arsenious sulphide appears, from the foregoing experiments, to be able to form both highly acid and highly basic salts.

W. R.

**Notes on Vanadium Compounds.** By B. W. GERLAND (Chem. News, xxxiv, 2—4).

I. VANADIC SULPHATES.—1. (*a.*) *Insoluble Modification.*—This is obtained by dissolving vanadic pentoxide in dilute sulphuric acid in presence of reducing agents such as alcohol, sulphurous acid, &c. In the resulting solution, after evaporation, strong sulphuric acid produces a precipitate. This precipitate, after cooling and removal of excess of acid, was washed with alcohol and dried. It yielded a pale blue, needle-shaped, hygroscopic salt, soluble in water, and having the approximate composition $V_2O_4.3SO_3.4H_2O$.

1. (*b.*) *Soluble Modification.*—A concentrated solution of the above salt is mixed with alcohol, and after repeated washings a transparent blue mass remains having the composition $V_2O_4.3SO_3.15H_2O$. It is hygroscopic.

The aqueous solutions of both these modifications are identical.

A mixture of vanadic and potassic sulphates yielded a double sulphate of pale blue colour uncrystallisable and not hygroscopic.

2. (*a.*) $V_2O_4.2SO_3$. *Insoluble Modification.*—Prepared by boiling the above described salts with sulphuric acid, when it becomes precipitated as a heavy powder of greyish-green colour. The crystals are insoluble in water, hydrochloric acid, and sulphuric acid, but are dissolved when heated with water in a sealed tube to between 150° and 200°, and are decomposed by dilute alkaline solutions, with formation of brown hydroxide.

2. (*b.*) $V_2O_4.2SO_3.10H_2O$. *Soluble Modification.*—The solution obtained by heating 2 (*a.*) with water in sealed tubes, when mixed with alcohol and evaporated, yielded crystals of the above composition. Heated with hydriopotassic sulphate, the vanadium sulphates fuse without decomposition.

II. META-VANADIC ACID, $HVO_3$.—A cold saturated solution of copper sulphate is mixed with a strong solution of ammonium chloride in large excess. Ammonium vanadate in saturated solution is then added until a permanent precipitate appears, and the mixture is slowly heated to 75°, when gold-like scales of vanadic acid form and continue to do so for some hours. The precipitate is collected, treated with dilute sulphuric and sulphurous acids, washed with water and dried, but it still retains traces of ammonia. Meta-vanadic acid may also be obtained by precipitating ammonium vanadate with a copper salt, separating the precipitated cupric vanadate, and warming the remaining solution. The acid thereupon separates and may be purified from copper by hydrochloric acid.

Meta-vanadic acid is highly hygroscopic, suffers no change at 150°, but loses its water at higher temperatures. The filtrate from the copper vanadate, if kept for ten days, remains clear on boiling.

The orginal liquor evaporated in a thin layer at low temperature leaves a crystalline residue; this forms with cold water a clear solution which, when heated to 75°, deposits meta-vanadic acid in scales.

The liquor, when dialysed, parted with all its salts save the vanadic acid; the remaining solution yielded no scales on boiling.

F. J. L.

**New Researches on Gallium.** By LECOQ DE BOISBAUDRAN (Compt. rend., lxxii, 1076).

PURE gallium melts at 29·5° and liquefies on being held between the fingers. It remains in a state of superfusion with great facility, which explains how a globule of it may remain liquid for several weeks, even though the temperature may occasionally fall nearly to zero. When solidified the metal is somewhat hard, even at a temperature only a few degrees short of its fusing point; it possesses, however, some malleability and may be cut with a knife. When melted it adheres to glass, forming a mirror which is whiter than that produced by mercury. Heated to redness in air gallium oxidises only superficially and does not volatilise. Hot nitric acid dissolves it, but the cold acid scarcely attacks it. The density of the metal is 4·7 at 15°, determined as nearly as possible, on 0·064 gram weight of it.

The metal was obtained by electrolysing an ammoniacal solution of gallium sulphate; its hydrochloric acid solution gave the spectroscopic lines of gallium, and much more feebly those of zinc.

The oxide of gallium is very soluble in potash but only slightly so in ammonia, but the metal deposited from the latter is solid and from the former it is liquid.

The metal is deposited upon the platinum negative electrode in minute globules, from which dilute hydrochloric acid dissolves it with rapid liberation of hydrogen. The hydrochloric solution was not coloured by potassium iodide, ammonia, or ammonium sulphide.

C. H. P.

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**On Nickel obtained from Minerals from New Caledonia.** By P. CHRISTOFLE and H. BOUILHET (Compt. rend., clxxxiii, 29—31).

THE nickeliferous ores of New Caledonia are free from sulphur and arsenic. They are hydrosilicates of magnesia and nickel. The iron found in them is not in combination and appears to occur only in small veins and nodules. The average composition of the ores is as follows:—

| $H_2O$. | $SiO_2$. | $Fe_2O_3$. | NiO. | MgO. | | |
|---|---|---|---|---|---|---|
| 22 | 38 | 7 | 18 | 15 | = | 100 |

The metal extracted from these ores, whether by the wet or the dry process, is of excellent quality. That obtained by the wet process flattens under the hammer, without breaking. The following are analyses of the metal reduced (I) by the wet process and melted, and (II) by a mixed wet and dry process, and melted:—

| | Ni. | Si. | C. | Mn. | Cu. | Fe. | | |
|---|---|---|---|---|---|---|---|---|
| I ... | 97·75 | 0·54 | 1·25 | 0·36 | — | — | = | 99·90 |
| II.... | 98·00 | 0·13 | — | — | 0·50 | 1·60 | = | 100·23 |

German silver containing 15 per cent. of nickel is remarkable for its malleability, homogeneity, and whiteness. It may be drawn into wires or rolled into sheets of any thickness, and is well adapted for ornamental work.

J. R.

**Preparation and Properties of the Chlorine and Bromine Compounds and the Oxide of Gold.** By JULIUS THOMSEN (J. pr. Chem. [2], xiii, 337—347).

*The Double Chloride of Gold*, $AuCl_3.AuCl$.—This compound is easily obtained by the action of dry chlorine gas on gold in the spongy state, best prepared by precipitation with sulphurous acid, boiling with nitric acid, washing, and drying at 170°. The double chloride is a dark-red, hard body, which may be easily reduced to a fine powder. It is very hygroscopic, and is decomposed by water into chloride and subchloride, which may be separated from each other by a rapid filtration. The subchloride, however, is decomposed on washing into the chloride and metallic gold. The double chloride undergoes decomposition at 250°, with escape of chlorine and volatilised anhydrous chloride.

*The Anhydrous Chloride*, $AuCl_3$ is rapidly and easily prepared by decomposing the double chloride with water. The solution should be very concentrated, since dilute solutions of gold chloride suffer decomposition on evaporation. . Gold chloride is very deliquescent in damp air, and very soluble in water, forming a dark-red solution. It is also obtained as a bye-product, during the preparation of the double chloride, in the form of large reddish-brown leaf-like crystals.

*Crystalline, Hydrated Chloride*, $AuCl_3 + 2H_2O$.—When the solution of the neutral chloride is evaporated down till a pellicle forms on the surface, it forms, in dry air, large dark orange-coloured brittle, often tufted crystals, which are very hygroscopic and deliquesce in air. The hydrated chloride, however, loses its water completely in dry air at the ordinary temperature.

*The Subchloride*, $AuCl$.—When the anhydrous chloride is exposed to a temperature of 185°, it is changed into the sub-chloride.

*The Double Bromide*, $AuBr_3 + AuBr$, prepared by acting on spongy gold with bromine, is an almost black body, which does not deliquesce in damp air. It is decomposed at 115° essentially into bromine and sub-bromide, but it is difficult to prepare the sub-bromide in this way. It is slowly soluble in water with absorption of heat and formation of bromide and sub-bromide; the latter, however, suffers a further decomposition. It is more quickly decomposed by acids. Anhydrous ether decomposes it quickly in part, since the bromide dissolves more quickly; the final products are bromide and metallic gold.

*Anhydrous Bromide*, $AuBr_3$.—Prepared by acting on the double bromide with ether in a flask in which the liquid may be cooled by exhausting the air. A drop exposed on a glass plate till the ether has evaporated, shows under the microscope a dark, very fine layer of regular crystals. In preparing large quantities of the bromide, the concentrated solution must be evaporated at a very low temperature. Gold bromide forms a dark-brown powder which is anhydrous and not deliquescent. It is perfectly soluble in water and ether, and the solutions are almost black when concentrated. An aqueous solution of gold bromide is easily prepared by shaking up the double bromide for some time with warm water. A solution of the bromide is re-

duced by sulphurous acid, with formation of sub-bromide and then of metallic gold.

*Bromide of Hydrogen and Gold*, $AuBr_4H + 5H_2O$.—This body deserves attention on account of its easy preparation, its stability in air, and its tendency to crystallisation. It is prepared by adding bromine to spongy gold, and as soon as the reaction is ended, a molecule of hydrogen bromide (sp. gr. 1·38) for each atom of gold, and then bromine till the gold is perfectly dissolved. On standing in a cool place for a time, the whole becomes a crystalline mass. The crystals are large, acicular, of a dark cinnabar colour, brittle, and stable in air. At a temperature of 27°, this salt melts in its water of crystallisation.

*The Sub-bromide*, AuBr.—When the bromide of hydrogen and gold is heated in a porcelain dish, so that the heat is applied to the bottom without affecting the sides, water and hydrogen bromide escape, and the solid residue consists chiefly of bromide; the mass is then exposed to a temperature of about 115°, with occasional stirring for some hours. Bromine and some hydrogen bromide escape, the colour finally changes to a yellowish-grey, and the mass is greasy to the touch. Analysis shows that it then consists of AuBr. The sub-bromide is stable in air, friable, and insoluble in water. At a higher temperature, it is resolved into bromine and metallic gold. It is converted by hydrobromic acid into hydrogen-gold bromide and the metal.

*The Hydrated Oxide.*—A very dilute solution of gold chloride, about 1 molecule of chloride to 800 molecules of water, is warmed with 3 equivalents of sodium hydrate. The liquid becomes first bright yellow and then dark brown. A solution of sodium sulphate is added, and this precipitates the hydrated oxide of a dark brown colour. This oxide is insoluble in water, but dissolves easily in very dilute hydrobromic acid, more slowly in very dilute hydrochloric acid.

G. T. A.

## Catalytic Action of Platinum. By Ernst. v. Meyer (J. pr. Chem. [2], xiv, 124—139).

This paper gives an account of the author's experiments as to the accuracy of the hypothesis of De la Rive, viz., that when platinum is placed in contact with a mixture of hydrogen and oxygen, a thin layer of oxide is formed, that this oxide is reduced by the hydrogen with reproduction of platinum, &c. The author showed in a previous paper (p. 40 of this volume), that when platinum acts on a mixture of hydrogen, carbon monoxide, and oxygen, the free oxygen unites by preference with the monoxide. The present experiments show that chemically combined oxygen, as in platinous and platinic oxide (or the hydrated oxide), exercises a totally different action on a mixture of carbon monoxide and hydrogen, and prove the incorrectness of De la Rive's hypothesis.

G. T. A.

# Mineralogical Chemistry.

**Mineralogical-crystallographical Notes.** By A. VON LASAULX (Jahrb. f. Min., 1876, 250—278).

*Melanophlogite, a new Mineral.*—This mineral was found by the author occurring on crystals of sulphur and cœlestine from Girgenti, accompanied by numerous small scalenohedrons of calcite. It has, however, only been observed on two specimens from Girgenti. It crystallises in the regular system, in small cubes having edges $\frac{1}{2}$ to 1 millimeter in length, sharply defined, and entirely free from modification. Twins occur similar to the well-known fluor-spar twins. Small groups of cubes, having sometimes a round shell-like appearance, were observed, the individuals being pushed into each other. Small chains composed of very minute cubes, project from the summits of the scalenohedrons of calcite, and under the microscope a distinct shell-like structure is observed on the faces of the cubes, with a difference in colour, being brown in one zone and lighter coloured in the other. The faces further appeared drusy, and exhibited an extremely slight step-like formation. The cubes resting upon calcite and cœlestine appear of a somewhat dark brown colour, whilst those resting on sulphur are generally colourless. The mineral has a strong vitreous lustre, and is almost transparent. Hardness, 6·5—7. Before the blowpipe it becomes first yellowish-grey, then grey-blue, and lastly, on being heated very strongly, blackish-blue, retaining its crystal form, but becoming at the same time brittle. Acids do not alter the black colour, nor can it be removed by the most intense heat: hence, it cannot be ascribed to compounds of sulphur or organic matter. By means of its property of becoming black before the blowpipe, the author was enabled to obtain tolerably pure fragments for analysis, separating it by this reaction from the cœlestine and calcite; the traces of the latter, still present, were removed by means of dilute hydrochloric acid, and the intermingled sulphur by bisulphide of carbon. No metals, excepting a trace of iron, could be detected in the borax bead, but a skeleton of silica was observed. Portions of the original non-ignited mineral lost 2·86 per cent. of water on ignition. An analysis of the mineral resulted as follows:—

| $SiO_2$. | $Fe_2O_3.Al_2O_3$. | SrO. | $SO_3$. | $H_2O$. |
|---|---|---|---|---|
| 86·29 | 0·7 | 2·8 | 7·2 | 2·86 = 99·85 |

From this analysis it appears not improbable that strontium sulphate (cœlestine) exists as an impurity in the mineral; and, leaving out the water, that the mineral is a rare combination of silicon and sulphur; but this must not be taken for granted until further analyses have been made. Melanophlogite occurs as a brown incrustation of minute cubes upon the macrodomes, the brachydome and brachypinacoïd of cœlestine. Between isolated crystals of cœlestine and sulphur, it occurs encrusting calcite. On sulphur-crystals, it is never found in

aggregates, but always in single crystals, having generally a light colour, and being sometimes nearly colourless.

*A new Pseudomorph.*—The author observed two large rhombohedrons upon a specimen of a finely granular mixture of magnetite, iron-pyrites, and calcite, from Traversella, which exhibited on one side a large crystal of scheelite, accompanied by numerous small, well-developed magnetite crystals and brilliant calcite crystals, all of them resting in a layer of greenish talc. Of the two rhombohedrons, one only was completely developed, the other being in a rudimentary stage. They were built up of a compact aggregate of small, brilliant, well-developed calcite crystals, of the combination $R.R^3.R^5.\infty P2$, the scalenhohedral faces being finely striated parallel to their combination edges with the prism. The primary rhombohedron R occurring independently, is of extreme rarity in the case of calcite; but as dolomite occurs in that form at Traversella, it was inferred by the author that the specimen under consideration was a pseudomorph of calcite after dolomite, as one of the rhombohedrons, exhibiting all its faces, was characterised by a peculiar shell-like structure, viz., the three lower faces were incrusted with a shell composed of irregularly disposed calcite crystals, and this shell-like incrustation was open near the lateral edges of the rhombohedron, whilst through this opening projected the three upper faces of the inner rhombohedral kernel. The innermost rhombohedron was cellular, showing many hollow spaces between the small crystals of which it was composed. The scalenohedral faces on the small crystals are distinguished by a distinct striation parallel to a terminal edge of the small rhombohedrons, and their presence seems to prove conclusively that the crystal is a pseudomorphous formation, being simply the primary rhombohedron R, whilst the small calcite crystals which build it up, exhibit several forms in combination. The mean of 30 measurements gave 107° 2′ as the terminal edge angle of the rhombohedron under consideration, a result which, taken in conjunction with the locality where it occurs, justifies the opinion that it is a pseudomorph of calcite after dolomite or magnesite. From the appearance of this pseudomorph the author contends that it cannot have arisen from the dolomite substance having been dissolved out and the hollow space filled up with calcite, nor could it have been formed by displacement, as the well-known law that "the substance of greater solubility cannot displace that of lesser solubility," shows, and innumerable examples of pseudomorphism prove. The absence of gypsum on the specimen seems also to show that the original dolomite crystal was not acted upon by a solution of gypsum (resulting in a double decomposition), or even by free sulphuric acid derived from the oxidation of the iron pyrites observed in the matrix. From the presence of scheelite, it appears highly probable, however, that tungstic acid was present in solution, and that, by its action upon the dolomite crystal, soluble tungstate of magnesium was formed and carried away, whilst calcium tungstate (which is insoluble) and calcite remained.

*Quartz with indented edges from Oberstein and Lizzo.*—After quoting the works on this subject by G. Rose, Weiss, G. vom Rath, Descloizeaux, Scharff, and Laspeyres, resulting in very contradictory state-

ments, the author proceeds at great length to give the results of his investigations, which are, briefly, as follows :—

*Amethyst from Oberstein.*—Druses from this locality were characterised by a thin coating or incrustation of chalcedony occurring on the faces of the two rhombohedrons in triangular patches, the indentations on the edges being extremely fine. There was not much difference observed between the faces of R and —R, although vom Rath expresses an opinion that (*Pogg. Ann., Einige Studien über Quartz*) the faces are entirely different, as they belong to two individual crystals, occurring together as penetration-twins, and accounts for the indentations observed on the edges by assuming that they are caused by the predominance of R over —R. In a previous communication, the author stated that he believed the true nature of the underlying amethyst crystals would be ascertained if once the chalcedony coating could be removed; and such proves to be the case, as he succeeded in removing it by means of a knife from the edges of the crystals, and then observed that none of the underlying forms exhibited any indentation of their edges, although they had done so previous to the removal of the chalcedony coating, and that their faces were identical in their physical characters. A section of one of the rhombohedron faces of the crystals, perpendicular to the vertical axis, was examined and found to enclose numerous long, brown, transparent, radiating, acicular crystals of the combination $\infty\breve{P}2$. $\infty\breve{P}\infty$. $\breve{P}\infty$, the enclosed mineral being pyrrhosiderite. These small crystals have grown in quartz having exactly the same appearance and optical properties as that of the quartz-kernel itself. A zone of chalcedony appears below this, and here the exterior indentation of the edges is observed, a fact which seems to prove that this indentation is not an abnormal growth, but arises rather from the retarding influence of the chalcedony coating upon the force of crystallisation, as it was observed that the incrustation adhered with greater tenacity to the faces than to the edges of the crystals. The author, therefore, concludes that vom Rath's deductions are not sufficiently borne out by facts, and ascribes the indentation to the above-mentioned cause.

*Quartz-crystals from Lizzo.*—These crystals are combinations of R and — R almost in equilibrium, the prism either not occurring at all, or else as an extremely fine modification of the horizontal edges of the two rhombohedrons. They are tolerably clear, but only slightly transparent, and are found in tertiary marl. All the faces are drusy, so that the signs of the two rhombohedrons cannot well be ascertained. Incrustations often occur on these faces, composed of small, completely developed individuals, and they cause fine re-entering angles upon the terminal and lateral edges of the large individuals. This indentation cannot arise through the incomplete union of two individuals according to a twin law, as in that case the indentation would be observed only on the terminal edges. It might arise, however, by an incrustation occurring upon all the faces of the crystal simultaneously, and the specimens from Lizzo show a parallel aggregation of drusy crystal individuals, completely covering the face of a large individual. Leydolt, in 1854 (*Ueber eine neue Methode die Struktur und Zusammensetzung der Krystalle zu untersuchen, mit besonderer Berücksichtigung der*

*Varietäten des rhomboëdrischen Quartzes*) enunciated the two following laws :—

1. By the action of a slow solvent, symmetrical depressions occur on natural or artificial crystals expressing exactly by their position and form the crystal system to which the body belongs.

2. These depressions are equal and parallel if the mineral is a perfectly simple one, but they differ in position as the construction is regular or irregular.

According to the same author, depressions with shining faces occur on the faces of the hexagonal pyramid on simple crystals, having a parallel position on one and the same face, and occurring on R and — R. These depressions correspond exactly with the positions of the two rhombohedrons. The manner of the construction of twins is also made apparent by the above method, although previous to the etching, no trace of any difference in the individual faces could be observed. Similar phenomena were observed by Leydolt on the etched surfaces of crystal plates, cut at right angles to the vertical axis, and extremely small and fine etched figures were impressed upon isinglass films and then examined under the microscope. Von Lasaulx used these methods in his examinations of quartz. Sections at right angles to the vertical axis and exactly through the lateral edges of two crystals were prepared (one of amethyst from Oberstein, the other of quartz from Lizzo, both distinctly exhibiting indentations on the edges) and etched by the action of aqueous hydrofluoric acid (50 per cent. of acid). The amethyst crystal section was almost etched through in the course of three hours, and appeared milk-white, whilst that of the Lizzo quartz showed only a slight opacity on the surface. With the amethyst the action was in direct relation to the form; the hexagonal plate appeared like a six-rayed star, the sides being completely eaten away, whilst in the direction of the axes it was intact and projected outwards like the spokes of a wheel. Etched figures could be obtained only upon the innermost quartz-kernel of the amethyst, and were then quite as distinct as those obtained with the quartz from Lizzo. The action was stronger on the edges than on the indentations, the latter appearing slightly opaque at first, but eventually becoming deeper and broader. A small crystal of Lizzo quartz was etched whole, and small, new faces were observed, corresponding with those previously obtained by Leydolt and Descloiseaux, and no doubt belonging to $-\frac{1}{2}$R. No twin formation was observed with indented Oberstein amethysts, or even with the quartz from Lizzo, although isinglass impressions seem to point to an irregular twin formation, which however has nothing to do with the indentations of the edges. The sextants of the section do not show that it is composed of two halves of two rhombohedrons of opposite signs, but only of secondary portions of a single individual turned about (eines verwendeten Individuums). Descloizeaux states that penetration-twins of quartz of complete regularity and symmetry are extremely rare, but von Lasaulx corrects this by stating that quartz never occurs as a penetration-twin with its components consisting of complete symmetrical individuals. All quartz twins are composed of many irregularly disposed lamellæ or crystal portions, whose structure can be ascertained only by optical examination or by etching. The

author's conclusion therefore is, that indentations on quartz crystals are only the result of abnormal development.

*Cuprite Crystals with Indented Edges.*—Small drusy crystals of cuprite from Redruth, exhibited a distinct indentation on their edges. The predominating form was the octohedron $\infty$ O, occurring very slightly developed, also occasionally 202 and $\infty$ 02. On the octohedral faces very thin, small, octohedral faces were observed, forming a thin shell over their surface. When two of these sub-individuals project past the combination-edge between O and $\infty$ O a re-entering angle is formed at the bottom of which the strongly striated face of $\infty$ O appears. This peculiar shell-like aggregation of sub-individuals (having the same form as the crystal-kernel) seems to occur mostly on the opposite-lying faces to an octohedral solid angle, the other faces being unaltered. Some crystals exhibit successive shell-like formations, and it is then observed that the lower ones combine together and again develop the crystal-kernel symmetrically, that is obliterating any indentations which may have existed previously on that portion of the crystal.

C. A. B.

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## On the Chemical Constitution of Maxite. By H. Laspeyres (J. pr. Chem. [2], xiii, 370—385).

The author has re-examined the mineral which he named maxite some years ago. It is an ore of lead from Sardinia, and is probably a variety of leadhillite. The empirical formula is $H_{10}Pb_{18}C_9S_5O_{56}$. It may be considered to consist of—

| | | |
|---|---|---|
| 9 molecules of ortho-carbonic acid, | $H_4CO_4$ | $= H_{36}C_9O_{36}$ |
| with 5 ,, sulphuric acid, | $H_2SO_4$ | $= H_{10}S_5O_{20}$ |
| | | $H_{46}C_9S_5O_{56}$ |

in which 36 atoms of hydrogen have been replaced by lead.

G. T. A.

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## Composition of Shepard's Hermannolite. By R. Hermann (J. pr. Chem. [2], xiii, 386—395).

This new mineral was discovered a few years ago in Connecticut, imbedded in granite. It crystallises in thick four-sided prisms with pyramidal terminations. It is black, opaque, and furnishes a dark-brown powder. The fracture is small-conchoïdal, smooth and bright. Spec. gravity 5·32. Thin splinters heated in the blowpipe flame become rounded at the edge. The mineral gives a brown glass with borax, and on addition of saltpetre the manganese reaction shows itself. On heating it on charcoal with soda, traces of tin are found.

The formula of the mineral is $2(2RO.NbO_2) + RO.Me_2O_5$:

$$RO = (MnO,FeO)\,;\ Me_2O_5 = (\tfrac{1}{4}Ta_2O_5.\tfrac{3}{4}Il_2O_5).$$

The allied minerals are—

| | | |
|---|---|---|
| Columbite .... | $RO.Me_2O_3.Me_2O_3$ .... | [Me = Nb,Il,Ta] |
| Ferro-ilmenite .. | $RO.2MeO_2.MeO_2$ .... | [Me = Nb,Il,Ta] |
| Tantalite ..... | $(2RO.3MeO_2) + 4(RO.2Ta_2O_3)$ | [Me = Il,Sn,Ti] |

G. T. A.

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## The Nickel Ore of New Caledonia called "Garnierite."

By J. GARNIER (Compt. rend., lxxxii, 1454—1455).

THE nickel ores of New Caledonia are now actively worked. They are not arseniosulphides of nickel, like those hitherto utilised, but silicates of nickel and magnesium. These ores occur imbedded in serpentine masses, which are very abundant in various parts of the island, and associated with euphotides, diorites, amphibolites, &c. Sometimes it shows itself on the different rocks as a green coating; at other times it penetrates and colours them more or less intensely, or it forms regular veins, which sometimes attain the thickness and regularity of lodes. The nickel is accompanied by iron, chromium, and cobalt. These metals, especially the two former, are present in great abundance, their mode of occurrence being analogous to that of the nickel, excepting that at those places where cobalt occurs. This latter metal is associated with manganese, forming masses more or less voluminous and pure, in the midst of brittle sandy rocks, formed from the *débris* of felspar and dolomite. The nickel ore approaches very near to the "pimelites."

D. B.

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## Examination of some Minerals from Chile.

By A. DOMEYKO (Compt. rend., lxxxiii, 451—452).

*Chloriodide of Silver and Mercury.*—This mineral is amorphous, and has a yellow colour resembling that of tocornalite (iodide of silver and mercury). It is reduced incompletely and with difficulty by zinc and dilute acid, but is easily decomposed by sulphurretted hydrogen. It is associated with an insoluble gangue containing barium and lead sulphates.

From the proportions in which the various elements are found, it is probable that the mercury is combined with the iodine, and the silver with the chlorine, thus:

| | |
|---|---|
| Silver chloride..... | 46 |
| Mercurous iodide ..... | 54 |
| | 100 |

*Polybasic Sulphates of Copper.*—Ordinary cupric sulphate is occasionally found pure, but is usually associated with ferric sulphate, forming a species of cupro-ferric alum, of a pale blue colour.

In the valley of San Francisco, opposite Santiago, are copper mines abounding in pyrites and sulphates. One of these sulphates has been examined; it is of a sky-blue colour, and has a fibrous structure; in

composition it resembles the alums, the alumina being replaced by ferric oxide and the alkaline base by cuprous oxide. The proportion of water is variable.

H. W.

## Aragonite found on the Surface of a Meteorite.

By J. LAWRENCE SMITH (Compt rend., lxxxii, 1505—1507).

THIS paper is a study of some meteoric masses originating from a region of Mexico, called the "Desert," situated in Cohahiule and Chihuahua (two provinces in the north), extending over 400 miles from the east to west and 500 miles from the north to south, along the banks of the Rio Grande. These regions, rich in meteoric irons, have been studied by Burckhardt, of Bonn. In 1854 three of these masses were described by the author. Two of them were brought to the United States, weighing 125 kilos. and 680 kilos. respectively. In 1868 eight others were described and added to the above. In 1871 a description of a larger mass, weighing about 3,500 kilos., was given, originating from the west of the region (near El-Para). The total weight of meteoric masses found in this country amounts to 15,000 kilos., a weight which surpasses that existing in various collections of meteorites.

On examining the above-mentioned eight masses in 1868, the author observed on the surface of two a white incrustation, which was not examined more closely at the time, and it is only some months since that these masses were placed at his disposal for investigation.

On the surface of one of these iron masses weighing 210 kilos., a small quantity of an incrustation was noticed which covered about 15 square centimeters of the surface of the body; another, weighing 275 kilos., showed an incrustation occupying more than 200 square centimeters of surface. The substance is so firmly attached to the iron, that if broken it separates a portion of the oxidised iron. Its thickness varies between 1 and 5 mm. It is very hard, and easily scratches calcspar. Its surface is irregular and granular. If broken perpendicularly to the iron surface, it can be easily polished. On several pieces an irregular and undulated structure with yellow and dark brown veins was observed. It effervesces with acids. The following is the composition of the mineral:—

| $CaCO_3$. | $Fe_2O_3$. | MgO. | Insoluble. | Water. | | |
|---|---|---|---|---|---|---|
| 93·1 | 1·0 | trace | 4·6 | 1·0 | = | 99·7 C |

With regard to the formation of this incrustation, the author is convinced that it was occasioned after the fall of the stone. The spot where this mass was found is situated in a valley between two parallel mountain ranges, at a distance varying from 1—3 miles. The foot of the mountains and the hills and plains show large calcareous deposits. The plain is at several places excavated by deep ravines. Several specimens of iron have been found in the middle of the deposits and in the sand. Those at the bottom of the ravines are covered with water during the heavy rains.

D. B.

**On "Sulphuric Acid Springs" of the Büdösberg, and on the Büdös Cavern.** By ANTON FLEISCHER (Deut. Chem. Ges. Ber., ix, 995—998).

ON the south-western slope of the Büdösberg, at the height of 1,070 meters, is a cavern in which there collects a stratum of gas, varying in the course of the day from 1·5 to 1·9 meters in depth. This gas consists of carbon dioxide together with a little hydrogen sulphide. The sides of the cavern to the depth of the gas stratum are covered with a yellow deposit of sulphur.

South-west of the cavern, about 75 meters distant, occur three "sulphuric acid springs." The water of these springs, the flow of which is attended by the evolution of large quantities of gas, was found to contain free sulphuric acid, the other mineral constituents being chiefly alumina, ferric oxide, and lime. The author promises a fuller account of these springs hereafter.

J. R.

**Composition of the Ochrey Deposit from the Mineral Water of Birresborn.** By H. VOHL (Deut. Chem. Ges. Ber., ix, 987).

THE deposit is of a fine brown colour after drying. When washed with distilled water and dried at 100°, it contains, after deducting matters insoluble in hydrochloric acid, which amount to 22·78 per cent. of the whole deposit—

| | |
|---|---|
| Ferric oxide | 83·2535 |
| Lime (carbonate) | 3·7414 |
| Magnesia (carbonate) | 1·3283 |
| Alumina | 0·0318 |
| Manganese protoxide | 0·0665 |
| Silica | 0·8407 |
| Phosphoric acid | 2·5324 |
| Arsenious acid | 1·3388 |
| Lithia | traces |
| Cupric oxide | traces |
| Water and organic matter (by diff.) | 6·8666 |
| | 100·0000 |

J. R.

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**Note on a Hydrated Silicate of Aluminium deposited by the Hot Spring of Saint Honoré (Nièvre) since the Roman Age.** By A. DAUBRÉE (Compt. rend., lxxxiii, 421—423).

THE mineral consists of a white substance of laminated structure, transparent in thin sections, and capable of good polish. It adheres to the tongue, and is more coherent than chalk or mountain-meal. It acts on polarised light. On examining the polished fracture closely, minute, dark, opaque particles can be distinguished, which can be

easily detached from the matrix. Between the layers small crystalline particles of gypsum may be seen, which probably impart to the mineral its action on polarised light.

On analysis the following numbers were obtained:—

| $SiO_2$ | $Al_2O_3$. | $Fe_2O_3$. | CaO. | MgO. | $H_2O$. | | |
|---|---|---|---|---|---|---|---|
| 76·6 | 12·6 | 2·3 | 1·8 | trace | 6·3 | = | 99·6 |

Another analysis showed the presence of alkaline chlorides and organic salts. The mineral probably is precipitated by chemical action from the hot springs, which have a temperature of 31°. The mineral is probably a mixture of several species; in composition it approaches nearest to pyrophyllite and pagodite.

H. W.

**Currents at the Mouths of Rivers: a Contribution to our knowledge of Ocean Currents.** By F. L. Ekman (Deut. Chem. Ges. Ber., ix, 857).

In the case of rivers falling into the sea, an under-current of perfectly salt water, according to the depth, the nature of the bottom, &c., runs up to a greater or less distance in the opposite direction. The Gotha, for instance, half a (Swedish) mile before its entrance into the sea has water at the depth of two fathoms of almost the same saltness as sea water at a similar depth a mile and three-quarters from its mouth. Currents in general are caused not only by the difference in specific gravity, but also by the distribution of rain-fall, evaporation, heat, &c., which produce surface changes.

G. T. A.

**Examination of the Organic Matter found in Ancient Soils.** By C. Husson (Compt. rend., lxxxiii, 454—457).

The author in this paper arrives at the following conclusions:—1st. That bitumens having a tarry odour are of vegetable origin. 2nd. That bitumens having a fetid odour, like that of Dippel's oil, are of animal origin. 3rd. That these latter are in the secondary and tertiary strata, the last remains of the animal substance which is found already very much changed in diluvium, and exists in great part in the state of ossein in the soil of bone-caves.

H. W.

# Organic Chemistry.

## On the Magnitude of the Atomic Volume, and the Specific Gravity of Organic Compounds. By R. HERMANN (J. pr. Chem. [2], xiii, 395—418).

THE solid elements in a state of combination may possess different properties from what they do in the free state, and their atoms may suffer a change in volume, just as is the case in the allotropic modifications of some elementary bodies. Carbon above all other bodies exhibits a readiness to change its atomic volume. Every single member of a hydrocarbon group contains carbon differing in atomic volume and quantivalence from the carbon of all the other members of the same group. This is produced by the pairing of primitive carbon-atoms of different atomic volume in the most varied proportions. Methane, for instance, contains carbon with the normal atomic volume $\frac{C}{1}$ and quantivalence IV: its steric formula therefore is $\frac{C}{1}\frac{H_4}{1}$. Ethane contains $\frac{C}{1}$ paired with $\frac{C}{0\cdot5}$ and its quantivalence is only II. Its formula is $\frac{C_2}{0\cdot75}\frac{H_6}{1}$. Propane contains $\frac{C}{1}\frac{C_2}{0\cdot5}$: its formula is $\frac{C_3}{0\cdot66}\frac{H_8}{1}$.

(1.) *Estimation of the Magnitude of the Atomic Volume of Carbon in the Hydrocarbons.*—The atomic weights of two neighbouring members of the group $C_nH_{2n+2}$ differ by $CH_2 = 14$; their atomic volumes by 16·75. The link (paarling) of the hydrocarbons of the methane group is therefore $CH_2$, with the atomic volume 16·75. Since all the hydrocarbons contain normal hydrogen $\frac{H}{1}$ with the atomic volume 6·5, the atomic volume of the carbon in $CH_2 = 3\cdot75$, for $16\cdot75 - (2 \times 6\cdot5) = 3\cdot75 = \frac{C}{0\cdot5}$. The atomic volume of the gaseous members of the methane group may be obtained for the liquid state from the alcohols, which may be looked upon as liquid hydrocarbons in which an atom of hydrogen has been exchanged for hydroxyl, $\frac{H}{1}\frac{O}{1\cdot5}$. Since $\frac{O}{1\cdot5} = 7\cdot5$, it is only necessary to subtract this number from the corresponding alcohols to obtain the atomic volume of the hydrocarbon in the liquid state, thus:—

| | | Observed. | Calculated atomic volume. |
|---|---|---|---|
| Methane..... | 40·10 − 7·5 = | 32·60 | 33·50 |
| Ethane ..... | 57·07 − 7·5 = | 49·57 | 50·25 |
| Propane..... | 74·50 − 7·5 = | 67·00 | 67·00 |

Since the calculated atomic volume of liquid methane is 33·50, the atomic volume of the carbon therein is $33\cdot50 - (4 \times 6\cdot5) = 7\cdot50$, and the steric formula is $\frac{C}{1}\frac{H_4}{1}$.

$$\text{Ethane becomes } \frac{C}{1}\ \frac{C}{0{\cdot}5}\ \frac{H_6}{1} = 50{\cdot}25$$

$$\text{Propane.....} \frac{C}{1}\ \frac{C_2}{0{\cdot}5}\ \frac{H_8}{1} = 67{\cdot}00$$

To obtain less complex formulæ without altering the atomic volume of the carbon, we may add together the carbon atoms and volumes. In this way we get the following formulæ:—

$$\text{Methane .....} \frac{C}{1}\ \frac{H_4}{1}$$

$$\text{Ethane.....} \frac{C_2}{0{\cdot}75}\ \frac{H_6}{1}$$

$$\text{Propane .....} \frac{C_3}{0{\cdot}66}\ \frac{H_8}{1}$$

The atomic volume of the carbon, and the steric constitution of the members of the hydrocarbon groups may therefore be expressed by the following general formulæ:—

(1.) Methane group, $C_nH_{2n+2}$.

Primitive molecule $\frac{C}{1}\ \frac{H_4}{1}$.

Link (paarling) $\frac{C}{0{\cdot}5}\ \frac{H_2}{1}$.

Steric constitution $\frac{\frac{Cn}{2n+2}}{4n}\ \frac{H_{2n+2}}{1}$.

(2.) Ethene group, $C_nH_{2n}$.

Primitive molecule $\frac{C}{1}\ \frac{H_2}{1}$.

Link $\frac{C}{1}\ \frac{H_2}{1}$.

Steric constitution $\frac{\frac{C_n}{n}}{n}\ H_{2n}$.

(3.) Acetylene group, $C_nH_{2n-2}$.

Primitive molecule $\frac{C_2}{2{\cdot}5}\ \frac{H_2}{1}$.

Link $\frac{C_2}{1}\ \frac{H_4}{1}$.

Steric constitution $\frac{\frac{Cn}{2n+6}}{2n}\ \frac{H_{2n-2}}{1}$.

(4.) Valylene group, $C_nH_{2n-4}$.

(5.) Benzene group, $C_nH_{2n-6}$.

Primitive molecule $\frac{C_4}{1{\cdot}25}\ \frac{H_2}{1}$.

Link $\frac{C}{0{\cdot}5}\ \frac{H_2}{1}$.

Steric constitution $\frac{Cn}{\frac{n+6}{2n}}\ \frac{H_{2n-6}}{1}$.

(6.) Styrol, $C_nH_{2n-8}$.
(7.) Naphthalin, $C_nH_{2n-12}$.
(8.) Anthracene, $C_nH_{2n-18}$.

A table is given of the members of the methane group. The first five are as follows:—

| Name. | Steric formula. | Shortened formula. | At. weight. | At. vol. Calculated | At. vol. observed. | Sp. gr. Calculated. | Sp. gr. observed. |
|---|---|---|---|---|---|---|---|
| Methane .. | $\frac{C}{1}\ \frac{H_4}{1}$ | $\frac{C}{1}\ \frac{H_4}{1}$ | 16 | 33·5 | * 32·6 | 0·477 | * 0·490 |
| Ethane ... | $\frac{C}{1}\ \frac{C_1}{0{\cdot}5}\ \frac{H_6}{1}$ | $\frac{C_2}{0{\cdot}75}\ \frac{H_6}{1}$ | 30 | 50·25 | 49·5 | 0·597 | 0·606 |
| Propane... | $\frac{C}{1}\ \frac{C_2}{0{\cdot}5}\ \frac{H_8}{1}$ | $\frac{C_3}{0{\cdot}66}\ \frac{H_8}{1}$ | 44 | 67·00 | 66·9 | 0·656 | 0·657 |
| Butane.... | $\frac{C}{1}\ \frac{C_3}{0{\cdot}5}\ \frac{H_{10}}{1}$ | $\frac{C_4}{0{\cdot}625}\ \frac{H_{10}}{1}$ | 58 | 83·75 | 82·74 | 0·692 | 0·701 |
| Pentane... | $\frac{C}{1}\ \frac{C_4}{0{\cdot}5}\ \frac{H_{12}}{1}$ | $\frac{C_5}{0{\cdot}60}\ \frac{H_{12}}{1}$ | 72 | 100·5 | 100·5 | 0·716 | 0·716 |
| | | | Etc. | | | | |

(2.) *Atomic Volume and Specific Gravity of the Alcohols of the Hydrocarbons of the Methane Group.*—(*a.*) Monacid alcohols may be regarded as compounds of the corresponding hydrocarbons with an atom of oxygen.

$$\left[\frac{Cn}{\frac{2n+2}{4n}}\ \frac{H_{2n+2}}{1}\right] + \frac{O}{1{\cdot}5}.$$

* From alcohol.

| Name. | Formula. | At. wt. | Calculated at. vol. | Observed sp. gr. | Calculated sp. gr. |
|---|---|---|---|---|---|
| Methane alcohol. | $\frac{C}{1}\ \frac{H_4}{1}\ \frac{O}{1\cdot5}$ | 32 | 41·0 | 0·798 | 0·780 |
| Ethane " | $\frac{C_2}{0\cdot75}\ \frac{H_6}{1}\ \frac{O}{1\cdot5}$ | 46 | 57·75 | 0·806 | 0·798 |
| Propane " | $\frac{C_3}{0\cdot66}\ \frac{H_8}{1}\ \frac{O}{1\cdot5}$ | 60 | 74·5 | 0·806 | 0·805 |
| Butane " | $\frac{C_4}{0\cdot625}\ \frac{H_{10}}{1}\ \frac{O}{1\cdot5}$ | 74 | 91·25 | 0·824 | 0·811 |
| Pentane " | $\frac{C_5}{0\cdot60}\ \frac{H_{12}}{1}\ \frac{O}{1\cdot5}$ | 88 | 100·0 | 0·829 | 0·814 |

Etc.

(*b.*) Diacid alcohols (glycols) of the hydrocarbons of the methane group.

$$\left[\frac{Cn}{\frac{2n+2}{4n}}\ \frac{H_{2n+2}}{1}\right]\frac{O_2}{0\cdot5}.$$

| Name. | Formula. | At. wt. | Calculated at. vol. | Observed sp. gr. | Calculated sp. gr. |
|---|---|---|---|---|---|
| Ethane glycol... | $\frac{C_2}{0\cdot75}\ \frac{H_6}{1}\ \frac{O_2}{0\cdot5}$ | 62 | 55·25 | 1·125 | 1·122 |
| Propane " ... | $\frac{C_3}{0\cdot66}\ \frac{H_8}{1}\ \frac{O_2}{0\cdot5}$ | 76 | 72·00 | 1·051 | 1·055 |
| Butane " ... | $\frac{C_4}{0\cdot625}\ \frac{H_{10}}{1}\ \frac{O_2}{0\cdot5}$ | 90 | 88·75 | 1·019 | 1·014 |
| Pentane " ... | $\frac{C_5}{0\cdot60}\ \frac{H_{12}}{1}\ \frac{O_2}{0\cdot5}$ | 104 | 105·5 | 0·987 | 0·985 |

(*c.*) Polyacid alcohols of the hydrocarbons of the methane group.

Triacid (glycerin fats) $\left[\frac{Cn}{\frac{2n+2}{4n}}\ \frac{H_{2n+2}}{1}\right]\frac{O_3}{0\cdot5}$.

Tetracid (erythrite) $\left[\frac{Cn}{\frac{2n+2}{4n}}\ \frac{H_{2n+2}}{1}\right]\frac{O_4}{0\cdot5}$.

Hexacid (mannite, sorbite, dulcite) $\left[\frac{Cn}{\frac{2n+2}{4n}}\ \frac{H_{2n+2}}{1}\right]\frac{O_6}{0\cdot5}$.

*Glycerin.*—Composition $C_3H_8O_3$. Atomic weight, 92. Specific gravity 1·252. Hence the atomic volume is $\frac{92}{1\cdot252} = 73\cdot48$.

This atomic volume answers to the formula, $\frac{C_3}{0{\cdot}66}\ \frac{H_8}{1}\ \frac{O_3}{0{\cdot}5}$, which gives as the calculated sp. gr. of glycerin 1·235. Glycerin is therefore the triacid alcohol of propane.

(3.) *Atomic Volume and sp. gr. of Monobasic, Monatomic acids (Fatty Acids)*—

$$\left[\frac{Cn}{\frac{n+2}{2n}}\ \frac{H_{2n-2}}{1}\ \frac{O_3}{2}\right] + \frac{H_2}{1}\ \frac{O}{1}.$$

| Name. | Formula. | At. weight. | Calculated at. vol. | Observed sp. gr. | Calculated sp. gr. |
|---|---|---|---|---|---|
| Formic acid. | $\frac{C_2}{1}\ \frac{H_2}{1}\ \frac{O_3}{2} + \frac{H_2}{1}\ \frac{O}{1}$ | 92 | 76·0 | 1·223 | 1·210 |
| Acetic „ | $\frac{C_4}{0{\cdot}75}\ \frac{H_6}{1}\ \frac{O_3}{2} + \frac{H_2}{1}\ \frac{O}{1}$ | 120 | 10·95 | 1·056 | 1·095 |
| Propionic „ | $\frac{C_6}{0{\cdot}66}\ \frac{H_{10}}{1}\ \frac{O_3}{2} + \frac{H_2}{1}\ \frac{O}{1}$ | 148 | 143·0 | 0·996 | 1·035 |
| Butyric „ | $\frac{C_8}{0{\cdot}625}\ \frac{H_{14}}{1}\ \frac{O_3}{2} + \frac{H_2}{1}\ \frac{O}{1}$ | 176 | 176·5 | 0·958 | 0·997 |
| | Etc. | | | | |

From the foregoing formulæ it is seen that the elements of the water are not to be reckoned with the elements of the acid anhydrides, since the oxygen of the water of constitution has a different volume from the oxygen of the anhydride. $(C_2H_4O_2)_2$ is therefore not equivalent to $\frac{C_4}{0{\cdot}75}\ \frac{H_6}{1}\ \frac{O_3}{2} + \frac{H_2}{1}\ \frac{O}{1}$.

Potassium acetate is not $C_2H_3O_2K$, but $\frac{C_4}{0{\cdot}75}\ \frac{H_6}{1}\ \frac{O_3}{2} + \frac{K_2}{0{\cdot}33}\ \frac{O}{1}$.

The basic oxides in these salts replace the constitutional water of the acids. It is not the metals of the bases which replace their equivalent of hydrogen of the acid.

(4.) *Atomic Volume and sp. gr. of the various Ethers of the Hydrocarbons of the Methane Group.* (*a.*) *Simple Ethers*—

$$\left[\frac{Cn}{\frac{2n+2}{4n}}\ \frac{H_{2n+1}}{1}\right]_2\ \frac{O}{2}.$$

By the action of an anhydrous acid on an alcohol, 2 atoms of the latter lose one atom of water, and the two atoms of $\frac{O}{1{\cdot}5}$ of the alcohol split up into $\frac{O}{2}$ and $\frac{O}{1}$, of which $\frac{O}{2}$ remains in combination in the ether, while $\frac{O}{1}$ joins with $\frac{H_2}{1}$ to form water.

| Names. | Formulæ. | At. wt. | Calculated at vol. | Observed Sp. gr. | Calculated Sp. gr. |
|---|---|---|---|---|---|
| Methyl ether ..... | $\left(\frac{C_5}{1}\frac{H_3}{1}\right)_2\frac{O}{2}$ | 46 | 64 | 0·718 | 0·718 |
| Ethyl „ ..... | $\left(\frac{C_2}{0{\cdot}75}\frac{H_5}{1}\right)_2\frac{O}{2}$ | 74 | 97·5 | 0·736 | 0·758 |
| Propyl „ ..... | $\left(\frac{C_3}{0{\cdot}66}\frac{H_7}{1}\right)\frac{O}{2}$ | 102 | 131·0 | 0·753 | 0·778 |
| Butyl „ ..... | $\left(\frac{C_4}{0{\cdot}625}\frac{H_9}{1}\right)_2\frac{O}{2}$ | 130 | 164·5 | 0·760 | 0·790 |
| | Etc. | | | | |

(*b.*) Compound ethers.

The atomic volume of the oxygen of inorganic acids varies when they are combined with ethers, thus:—

Nitric acid is $\frac{N_2}{1}\frac{O_5}{2}$ as in saltpetre.

Phosphoric acid is $\frac{P_2}{1}\frac{O_5}{0{\cdot}66}$ as in apatite.

Silicic acid is $\frac{Si}{1}\frac{O_2}{1}$ as in chrysolite.

| | At. wt. | At. vol. | Observed Sp. gr. | Calculated Sp. gr. |
|---|---|---|---|---|
| Ethyl ether $\left(\frac{C_2}{0{\cdot}75}\frac{H_5}{1}\right)_2\frac{O}{2} = E_2\frac{O}{2}$ | 74 | 97·5 | 0·736 | 0·758 |

*Compounds of Ethyl Ether with Inorganic Acids.*

| Names. | Formulæ. | At. wt. | At. vol. | Observed Sp. gr. | Calculated Sp. gr. |
|---|---|---|---|---|---|
| With nitrous acid | $E_2\frac{O}{2} + \frac{N_2}{1}\frac{O_3}{3}$ | 150 | 157·5 | 0·947 | 0·952 |
| „ nitric acid . | $E_2\frac{O}{2} + \frac{N_2}{1}\frac{O_5}{2}$ | 183 | 161·5 | 1·132 | 1·126 |
| „ carbonic acid | $E_2\frac{O}{2} + \frac{C}{1}\frac{O_2}{1{\cdot}5}$ | 118 | 120·0 | 0·975 | 0·983 |
| „ boracic acid | $3(E_2)\frac{O}{2} + \frac{B}{1}\frac{O_3}{1}$ | 292 | 315·8 | 0·887 | 0·924 |
| „ silicic acid.. | $2(E_2)\frac{O}{2} + \frac{Si}{1}\frac{O_2}{1}$ | 208 | 217·0 | 0·933 | 9·958 |
| | Etc. | | | | |

*With Inorganic Acids.*

| Names. | Formulæ. | At. wt. | At. vol. | Observed sp. gr. | Calculated sp. gr. |
|---|---|---|---|---|---|
| With formic acid . | $E_2 \frac{O}{2} + \frac{C_2}{1} \frac{H_2}{1} \frac{O_3}{2}$ | 148 | 155·5 | 0·916 | 0·951 |
| „ acetic acid . . | $E_2 \frac{O}{2} + \frac{C_4}{0{\cdot}75} \frac{H_6}{1} \frac{O_3}{2}$ | 176 | 189 | 0·906 | 0·931 |
| | Etc. | | | | |

(5.) *Atomic volume and sp. gr. of the Compounds of the Ether Hydrocarbons with other Elements.*—These hydrocarbons of the formula $C_nH_{2n+1}$ act like univalent positive elements (R), and combine with negative elements of different degrees of valency (X).

$$R\,X^{i};\ R_2\,X^{ii};\ R_3\,X^{iii};\ R_4\,X^{iv};\ R_6\,X^{vi}.$$

(*a.*) Combinations with $X^{i}$.

The halogens have a larger atomic volume when in combination with the hydrocarbons, than when they replace hydrogen atoms of hydrocarbons.

In compounds the values are $\frac{Cl}{1}\ \frac{Br}{1{\cdot}25}\ \frac{I}{1{\cdot}5}$.

In substitutions the values are $\frac{Cl}{0{\cdot}875}\ \frac{Br}{1}\ \frac{I}{1{\cdot}25}$.

Methane, for instance, $\frac{C}{1}\ \frac{H_4}{1}$ may be converted into monochloromethane $\frac{C}{1}\ \frac{H_3}{1}\ \frac{Cl}{0{\cdot}875}$, where $\frac{Cl}{0{\cdot}875}$ is substituted for an atom of hydrogen. Methyl $\frac{C}{1}\ \frac{H_3}{1}$ also can combine with chlorine to form methyl chloride $= \frac{C}{1}\ \frac{H_3}{1}\ \frac{Cl}{1}$.

(*b.*) Combinations with $X^{ii}$.

Among other compounds are sulphur ethide, $\left(\frac{C_2}{0{\cdot}75}\ \frac{H_5}{1}\right)_2 \frac{S}{1}$, and zinc ethide $\left(\frac{C_2}{0{\cdot}75}\ \frac{H_5}{1}\right)_2 \frac{Zn}{1}$.

(*c.*) Combination with $X^{iii}$, such as triethylamine, $\left(\frac{C_2}{0{\cdot}75}\ \frac{H_5}{1}\right)_3 \frac{N}{1}$.

(*d.*) Combination with $X^{iv}$, such as silicon ethide, $\left(\frac{C_2}{0{\cdot}75}\ \frac{H_5}{1}\right)_4 \frac{Si}{1}$.

(*e.*) Substitution of the hydrogen of ammonia by ether hydrocarbons.

Among these are such bodies as ethylamine, $\left.\begin{array}{c}\frac{H_2}{1}\\ \frac{C_2}{0\cdot75}\ \frac{H_5}{1}\end{array}\right\}\frac{N}{1}$.

The following are a few examples from the tables given :—

| Names. | Formulæ. | At. weight. | At. volume. | Observed sp. gr. | Calculated sp. gr. |
|---|---|---|---|---|---|
| Ethyl chloride ..... | $\frac{C_2}{0\cdot75}\ \frac{H_5}{1}\ \frac{Cl}{1}$ | 64·5 | 68·75 | 0·917 | 0·938 |
| Propyl bromide ..... | $\frac{C_3}{0\cdot66}\ \frac{H_7}{1}\ \frac{Br}{1\cdot25}$ | 123·0 | 91·75 | 1·349 | 1·340 |
| Hexyl iodide..... | $\frac{C_6}{0\cdot583}\ \frac{H_{13}}{1}\ \frac{I}{1\cdot5}$ | 212·0 | 147·75 | 1·445 | 1·434 |
| Mercuric ethide..... | $\left(\frac{C_2}{0\cdot75}\ \frac{H_5}{1}\right)_2\ \frac{Hg}{1}$ | 258·0 | 102·5 | 2·44 | 2·51 |
| Triethylphosphine ... | $\left(\frac{C_2}{0\cdot75}\ \frac{H_5}{1}\right)_3\ \frac{P}{1}$ | 118·0 | 144·5 | 0·812 | 0·816 |
| Stannic ethide ..... | $\left(\frac{C_2}{0\cdot75}\ \frac{H_5}{1}\right)_4\ \frac{Sn}{1}$ | 234·0 | 191·0 | 1·187 | 1·225 |
| Trichloromethane .... | $\frac{C}{1}\ \frac{H}{1}\ \frac{Cl_3}{0\cdot875}$ | 119·5 | 79·62 | 1·48 | 1·500 |
| Monobromomethyl ... | $\frac{C}{1}\ \frac{H_2}{1}\ \frac{Br}{1}$ | 102·0 | 45·5 | — | 2·241 |
| Ethylamine..... | $\left\{\begin{array}{c}\frac{C_2}{0\cdot75}\ \frac{H_2\ H_5}{1}\end{array}\right\}\frac{N}{1}$ | 45·0 | 64·25 | 0·696 | 0·700 |

G. T. A.

**Ultimate Action of Chlorine on Fatty Acids.** By F. KRAFFT (Deut. Chem. Ges. Ber., ix, 1085—1088).

HEXYL iodide, when treated with excess of chlorine, and afterwards heated to 240° with iodine trichloride, is ultimately converted into perchlorobenzene.

Trichloracetic acid, heated to 200° with iodine trichloride, yields perchloromethane, carbon dioxide, and hydrogen chloride.

Propionic acid similarly treated yields perchlorethane.

Isobutyric acid yields perchloropropane, with a little perchloromethane and perchlorethane.

J. R.

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**Action of Heat on Brominated Hydrocarbons.** By E. WALL (Deut. Chem. Ges. Ber., ix, 1049).

PERBROMOMETHANE is converted by prolonged boiling into perbromethane, perbromethene, and ultimately perbromobenzene. The same transformation is effected by heating it to 300°—400° in sealed tubes.

Allyl iodide heated to 240° with excess of bromine yielded perbromomethane, perbromethane, and a third body crystallising in white needles—probably perbromopropane.

J. R.

**Derivatives of Propyl and Propylene, &c.** By E. LINNEMANN (Deut. Chem. Ges. Ber., ix, 924—926).

I. ATTEMPTS to prepare propyl-glycol by the action of propylene dibromide or dichloride on potassium carbonate and water failed entirely, the only product of the action being a little monobromo- or monochloro-propylene. The behaviour of the haloïd derivatives of propylene towards aqueous potassium carbonate is, therefore, different from that of the corresponding ethylene-compounds.

II. Methylpropyl ketone (obtained by distilling a mixture of calcium acetate and butyrate), when subjected to the action of sodium amalgam, yields methylpropylcarbinol, $CH_3.CH(OH).CH_2.CH_2.CH_3$. This is a colourless liquid, having a burning taste and an odour of fusel oil. Its sp. gr. is 0·8239 at 0°, and 0·8102 at 20° (water at the same temperature being 1). It dissolves in 6 parts of cold water, and boils at 118·5°—119·5°. By oxidation with chromic acid it appears to yield acetic and propionic acids. These results seem to indicate that the methylpropylcarbinol thus obtained is identical with that of Saytzeff and Wagner.

III. Fumaric acid, when heated for 56 hours with aqueous soda-ley, is converted into a malic acid. The latter forms a syrupy liquid, which crystallises with difficulty, and is optically inactive. A solution of the calcium-salt of this acid prepared in the cold deposits, on boiling, microscopic hexagonal tables, which when dried over sulphuric acid, have the composition of neutral anhydrous calcium malate. The inactive malic acid thus obtained is being further investigated.

J. R.

**Mercaptan.** By P. CLÆSSON (Deut. Chem. Ges. Ber., ix, 854).

THE object of the investigation was to explain certain phenomena which occurred in the preparation of ethylsulphacetic ether, and the discrepancy of the results with those of Erlenmeyer and Lisenko, which might possibly be owing to some peculiar isomerism. Sodium sulphethylate, however, does not occur in isomeric forms. The abnormal results must have been due to the impurity of the chloracetic ether employed, and to the easy decomposition of sodium mercaptide with absorption of oxygen. Among the products of oxidation was an acid which is probably identical with the ether sulphurous acid of Maslitz. Some new mercaptides have been obtained, prepared in many cases like sulphides by means of sulphuretted hydrogen, and also a tetrasulphide and pentasulphide of ethyl. The author has also been investigating rhodanacetic acid and its isomerides.

G. T. A.

**A Reaction of Chloral.** By D. AMATO (Gazzetta chimica italiana, v, 427—430).

THE author found that when 5 parts of chloral were heated with 6 of iodic acid, in concentrated aqueous solution, at 120° in sealed tubes, carbonic anhydride was given off, and chloroform and iodine trichloride were produced, the latter remaining in solution in the water. It seemed possible that the iodine trichloride might be formed by the action of the iodic acid in presence of water on the chloroform produced by the splitting up of the chloral; or by the action of free iodine on water and chloroform. On trial, however, it was found that, in the former case, iodine trichloride was not formed below 200°, whilst in the latter no reaction took place even at that temperature.

C. E. G.

**A New Ether of Aceto-acetic Acid.** By O. EMMERLING and A. OPPENHEIM (Deut. Chem. Ges. Ber., ix, 1096).

THE authors have obtained *isobutyl aceto-acetate* in the same manner as the corresponding ethyl-compound was previously obtained by Oppenheim and Precht. It is a colourless liquid, of specific gravity 0·979 at 0° and 0·932 at 23°, and smells faintly of fennel. It boils about 203°, undergoing decomposition. The ether dissolves sodium rapidly, the resulting product being oxyuvitic acid, mixed with sodium isobutyrate and chloral.

J. R.

**Oxidation of Ethyl Aceto-acetate.** By O. EMMERLING and A. OPPENHEIM (Deut. Chem. Ges. Ber., ix, 1098).

THIS substance, when gently warmed with a dilute solution of potassium permanganate, is oxidised in the manner indicated by the equation :—

$$CH_3CO.CH_2COOC_2H_5 + 3O + 3KOH = CH_3COOK + C_2O_4K_2 + 2H_2O + C_2H_5OH,$$

the only acids formed being acetic and oxalic.

J. R.

**Action of Aniline on Ethyl Aceto-acetate.** By A. OPPENHEIM and H. PRECHT (Deut. Chem. Ges. Ber., ix, 1098).

THE reaction of these substances when heated together results in the formation of diphenylcarbamide, acetone, and alcohol, as shown in the following equation :—

$$CH_3CO.CH_2COOC_2H_5 + 2NH_2C_6H_5 = CO(NHC_6H_5)_2 + CO(CH_3)_2 + C_2H_5HO.$$

J. R.

## Derivatives of Dehydracetic Acid. By A. OPPENHEIM and H. PRECHT (Deut. Chem. Ges. Ber., ix, 1099—1102).

PHOSPHORUS pentachloride reacts with dehydracetic acid dissolved in phosphorus oxychloride, to form *dehydracetic chloride*, $C_8H_6O_2Cl_2$, that is dehydracetic acid in which two hydroxyl-groups are replaced by chlorine. This substance crystallises in reddish needles which melt at 101°. It is decomposed by distillation *per se*, but volatilises with water-vapour. When heated to 200° with water, it is converted into dehydracetic acid.

*Dehydracetamide*, $C_8H_7O_3.NH_2$, is obtained by evaporating a solution of dehydracetic acid in aqueous ammonia, or by evaporating a solution of the ethyl ether of the acid in alcoholic ammonia. It is a crystalline substance melting at 208·5° and dissolving easily in alcohol, ether, and hot water. It sublimes without decomposition.

*Dehydracetanilide*, $C_8H_7O_3.NHC_6H_5$, is formed by warming the acid with excess of aniline. It crystallises in white needles, which dissolve in alcohol and ether, melt at 115°, volatilise with aqueous vapour, and decompose when heated. It dissolves in dilute hydrochloric acid and forms a very unstable double salt with platinic chloride.

*Monochlorodehydracetic Acid*, $C_8H_7ClO_4$, obtained by passing chlorine into a solution of the acid in chloroform, crystallises in needles which melt at 93°.

*Monobromodehydracetic Acid*, $C_8H_7BrO_4$, is formed on heating a solution of the acid in chloroform to 30°—40° with bromine. It is a yellowish crystalline body melting at 134°.

J. R.

## Researches on the Derivatives of Acetylvaleric Ether. By E. DEMARÇAY (Compt. rend., lxxxiii, 449—51).

THIS body is prepared by the action of isopropyl iodide on ethylic aceto-sodacetate; the reaction is the following:—

$$CH_3—CO—CHNa—CO_2C_2H_5 + CH_3—CHI—CH_3 = NaI + \begin{array}{c} CH_3—CO—CH—CO_2C_2H_5 \\ | \\ CH_3—CH—CH_3. \end{array}$$

This compound, which is one of the acetylated derivatives of ordinary valeric acid, is a colourless fragrant liquid boiling between 200°—202°.

With one equivalent of bromine, an immediate decoloration of the bromine takes place, accompanied by abundant production of hydrobromic acid. The resulting oil is treated with alcoholic potash, dissolved in water, and excess of hydrochloric acid is added. Ether then takes up a body which is left on evaporation in long needles, coloured brown by foreign matter, which is got rid of by pressure between blotting-paper and crystallisation from boiling water. This body has acid properties, is slightly soluble in cold water, moderately soluble in hot water, very

soluble in alcohol, ether, and chloroform. It melts at 121°—123°, and boils with decomposition at 260°. Its composition approaches that of angelic acid, but its high boiling point tends rather to the conclusion that it is oxyvaleric anhydride.

With two molecules of bromine a solid acid is obtained having a yellow colour, melting at 184°, and boiling at 270°—280°. At this temperature it forms an oil which, in contact with water, reproduces the original acid. This acid is slightly soluble in cold, very soluble in hot water, also in alcohol and ether; very slightly soluble in chloroform. Analysis shows that it has the composition of oxyangelic acid. It combines with bromine to form crystals which have not been examined.

H. W.

## Isomalic Acid. By MAX SCHMOEGER (J. pr. Chem. [2], xiv, 77—84).

THE author has obtained this substance by replacing an atom of hydrogen in isosuccinic acid by hydroxyl. This replacement was effected by treating monobromo-isosuccinic acid with freshly precipitated silver oxide. The crude acid thereby formed was purified by converting it into lead salt and decomposing the latter with hydrogen sulphide. Analysis agreed with the formula $C_4H_6O_5$.

Isomalic acid is easily soluble in water, alcohol, and ether. Its crystalline form appears to be monoclinic. It begins to melt at 100°, undergoing decomposition. When heated to 160° it is resolved into carbon dioxide and lactic acid. Its salts, so far as they have been examined, are amorphous.

J. R.

## Derivatives of Normal Pyrotartaric Acid. By REBOUL (Compt. rend., lxxxii, 1502—1504).

*Zinc salt*, $C_5H_6O_4Zn$.—Anhydrous. Forms fine prismatic needles only slightly soluble in hot water. In spite of its slight solubility it is not precipitated when a concentrated solution of neutral sodium pyrotartrate is mixed with a solution of zinc chloride, but on heating the liquid to boiling, an immediate and abundant precipitation of needles of the zinc salt is the result. The ordinary neutral zinc pyrotartrate is said to be more soluble and to crystallise with $3H_2O$.

*The Copper salt (neutral)*, $2C_5H_6O_4Cu + H_2O$, forms a green solution which crystallises in groups of microscopic needles much less soluble in hot water than the former. It is obtained by double decomposition by passing a solution of sodium pyrotartrate with a solution of copper sulphate. The precipitate, which dissolves with difficulty in the excess of the copper salt, is soluble in an excess of the sodium pyrotartrate. Dried at 150° it loses 4·4 per cent. (calculated 4·6).

*The Lead salt*, $C_5H_6O_4Pb'' + H_2O$.—Lead nitrate is abundantly precipitated by a solution of neutral sodium pyrotartrate, the precipitate dissolving in an excess of the precipitant, but after some time the liquid becomes turbid and produces a copious, heavy, crystalline, white pre-

cipitate. It is less soluble in an excess of the lead nitrate, is nearly insoluble in hot water, and contains one molecule of water of crystallisation, which it does not lose at 145°—150°.

*The Silver salt*, $C_5H_6O_4Ag_2$, is obtained by double decomposition of silver nitrate and sodium pyrotartrate. It crystallises in fine needles which rapidly blacken in the air.

*Neutral Sodium salt*, $C_5H_6O_4Na_2$ at 150°. By saturating a hot solution of pure calcined sodium carbonate with one molecule of the normal acid, evaporating to a syrupy mass, exposing the mass to sulphuric acid under a jar, and drying at 145°—150°, this salt is obtained in the anhydrous state. It is very soluble in water, insoluble in alcohol, which precipitates it from its aqueous solution in the form of a white voluminous and gelatinous mass resembling aluminium hydrate.

*Acid Sodium salt.*—Obtained in long prismatic crystals by decomposing one molecule of pure anhydrous sodium carbonate with two molecules of pyrotartaric acid, evaporating the mixture on a water-bath. Dried at 150°—160° the salt retains $2H_2O$. Alcohol precipitates it from its aqueous solution. The precipitate resembles that of the neutral salt.

*Normal Ethyl Pyrotartrate*, $CO_2C_2H_5,CH_2—CH_2—CH_2—CO_2C_2H_5$.—Obtained by saturating a solution of the normal acid in absolute alcohol with hydrochloric acid gas. It forms a colourless liquid insoluble in water, very soluble in alcohol, has a specific gravity of 1·025 at 21°, shows no traces of decomposition at 236°—237°.

*Normal Pyrotartryl Chloride*, $COCl,CH_2—CH_2—CH_2,COCl$. — Obtained by the action of two molecules of phosphorus perchloride on one molecule of pyrotartaric acid. It forms a heavy liquid with an irritating smell, boiling without alteration at 216°—218°. Water decomposes it rapidly when hot, cold hydrochloric or pyrotartaric acid only very slowly. The same effect is produced by moist air. It turns brown in the air.

D. B.

## The Ferrocyanogen Compounds of the Metallic Acids.

By A. Atterberg (Deut. Chem. Ges. Ber., ix, 855—856).

These amorphous precipitates vary much in composition. They generally contain potassium, and the majority contain oxidised radicles. Tin, antimony, bismuth, alone give compounds free from oxygen. The acids examined were those of Mo, W, V, Nb, Ta, U, Ti, Tc, Sn, and the oxides of U, Sb, Bi. As examples might be adduced those of molybdic acid: $2MoO_3 + K_2(MoO_2)_3,2FeCy_6 + 20Aq$ and $2MoO_3 + K_6(MoO_2)$ $2FeCy + 12Aq$; of titanium: $K_2(TiO)_3 2FeCy_6 + 23Aq$ and $K_2(TiO)_{11}$ $6FeCy_6 + 110Aq$; of bismuth, antimony, and tin: $KBiFeCy_6 + 7Aq$; $Sb_4 3FeCy_6 + 25Aq$; $K_4Sn_{10} 11FeCy_6 + 230Aq$. No definite compounds of tungsten and tellurium could be obtained, and only those of the dioxide of vanadium. The compounds are arranged in groups according to the proportion between K and Fe ($K_3$ : Fe, $K_3$ : $Fe_2$, K : Fe, $K_4$ : $Fe_{12}$ or $Fe_{11}$, and those which contain no potassium).

G. T. A.

**On the Structure of Cyanic Acid Compounds.** By ANTON FLEISCHER (Deut. Chem. Ges. Ber., ix, 988—992).

AN argumentative paper in which the author maintains, in opposition to the criticisms of Claus, his previous conclusions as to the constitution of these compounds. The paper is not suited for abstraction.

J. R.

**On the Constitution of the Guanamines and Polymeric Cyanogen-compounds.** By M. NENCKI (Deut. Chem. Ges. Ber., ix, 1008—1013).

A THEORETICAL paper, not adapted for abstraction.

J. R.

**Derivatives of Uric Acid.** By H. B. HILL (Deut. Chem. Ges. Ber, ix, 1090—1094).

THE preparation and properties of methyluric acid have been described already (see this Journal, 1876, ii, 75). Alcohol added to a solution of methyluric acid in potash or soda throws down the salts—

$$K_2C_5H(CH_3)N_4O_3.3H_2O;$$
$$Na_2C_5H(CH_3)N_4O_3.3H_2O.$$

A solution of the acid in hot baryta-water deposits as it cools tufts of delicate needles of the barium salt—

$$BaC_5H(CH_3)N_4O_3.3\tfrac{1}{2}H_2O;$$

and a similar salt is formed with calcium hydrate. The following salts are formed by boiling the acid with the respective carbonates and precipitating the resulting solutions with alcohol:—

$$KC_5H_2(CH_3)N_4O_3.H_2O;$$
$$Ca[C_5H_2(CH_3)N_4O_3]_2.3H_2O;$$
$$Ba[C_5H_2(CH_3)N_4O_3]_2.4H_2O.$$

A solution of the mono-barium salt when mixed with sodium sulphate gives, on addition of alcohol, a precipitate of the salt $NaC_5H_2(CH_3)N_4O_3.H_2O$. Moderately strong solutions of the alkali salts gelatinise on cooling.

Methyluric acid in alkaline solution, when oxidised with a dilute solution of potassium permanganate, yields *methylallantoïn*, $C_4H_5(CH_3)N_4O_3$. This substance crystallises in monoclinic prisms resembling allantoïn. It melts at 225°, undergoing decomposition. A silver-compound, $AgC_4H_4(CH_3)N_4O_3$, is formed on adding silver nitrate and excess of ammonia to a hot solution of methylallantoïn: it crystallises in short prisms soluble in hot water. Methylallantoïn, when heated with strong hydriodic acid, yields urea and *methylhydantoïn*—

$$C_5H_8N_4O_3 + H_2 = CON_2H_4 + C_3H_3(CH_3)N_2O_2.$$

Methyluric acid is oxidised by potassium chlorate and hydrochloric

acid in the manner indicated by the following equation, the products being urea and *methylalloxan*:—

$$C_6H_6N_4O_3 + H_2O_2 = CON_2H_4 + C_4H(CH_3)N_2O_4.$$

Methylalloxan, when boiled with strong nitric acid, yields methylparabanic acid, $C_3H(CH_3)N_2O_3$.

J. R.

**On Hydurilic Acid.** By J. MURDOCH and OSCAR DOEBNER (Deut. Chem. Ges. Ber., ix, 1102—1106).

WHEN air-dried alloxantin is heated to 170° for three or four hours in a sealed tube, it is converted into the ammonium salt of hydurilic acid, carbon oxides and oxalic acid being formed at the same time. The product, when dissolved in water, acidified with hydrochloric acid, and evaporated, yields crystals of hydurilic acid. The decomposition is represented by the equation—

$$2(C_8H_4N_4O_7 + 3H_2O) = C_8H_6N_4O_6 + 4NH_3 + C_2H_2O_4 + 2CO + 4CO_2.$$

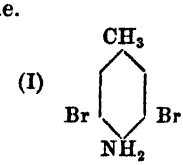
The same decomposition takes place when alloxantin is heated to 170° in an open vessel, but in this case most of the ammonia escapes, and free hydurilic acid is left.

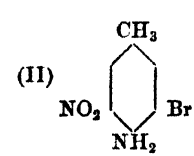
Crystallised air-dried alloxan, when heated to 170°, is likewise resolved into ammonium hydurilate, oxalic acid, and carbon oxides.

J. R.

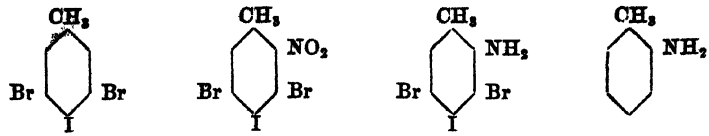
**Constitution of Benzene-derivatives.** By E. WROBLEVSKY (Deut. Chem. Ges. Ber., ix, 1055—1056).

WHEN the group $NH_2$ in dibromoparatoluidine (I) is replaced by iodine, dibromiodotoluene, $C_7H_5Br_2I$, is formed. The same product is obtained from bromonitrotoluidine (II) by replacing the group $NH_2$ by iodine, converting the group $NO_2$ into $NH_2$ and replacing the latter by bromine.

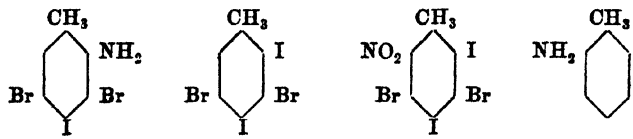



The author, by treating dibromiodotoluene with fuming nitric acid, obtained the compound $C_7H_4Br_2INO_2$. This body distils with steam and crystallises from acetic acid in large needles melting at 69°. By reduction with tin and hydrochloric acid it yields dibromiodotoluidine, $C_7H_4Br_2INH_2$, which crystallises from alcohol in needles melting at 64°. This last substance, when submitted to the prolonged action of sodium-amalgam, yields orthotoluidine, the acetyl-derivative of which melts at 120°. The successive steps in the process are represented thus:—




Again, dibromiodotoluidine was converted by Griess's method into dibromodiiodotoluene, $C_7H_4Br_2I_2$, which crystallises in prisms melting at 68°, and when treated with fuming nitric acid is converted into dibromodiiodonitrotoluene, $C_7H_3Br_2I_2NO_2$, a body which crystallises from alcohol in tables melting at 129°. The reduction of this substance gives rise to a solid amido-compound, which by prolonged treatment with sodium amalgam yields orthotoluidine as before.




J. R.

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## Action of Chlorine on Aromatic Substances.

By G. Ruoff (Deut. Chem. Ges. Ber., ix, 1048).

Most bodies of the aromatic series, when treated with iodine trichloride and heated, if necessary, to 360°, are converted into perchlorobenzene.

Phenol, cresol, thymol, and chloranil are converted with comparative facility into perchlorobenzene, the oxygen being eliminated as carbon dioxide. Resorcin, camphor, and oil of turpentine also yield perchlorobenzene; pyrogallic acid, however, gives chiefly perchlorethane. Azobenzene and the three phenylamines yield perchlorobenzene, as also do diphenylmethane, diphenylethane, anthracene, phenanthrene, and naphthalene, but in these latter cases the conversion is difficult. The most stable substance experimented on is diphenyl, which yields perchlorodiphenyl. Antimony pentachloride acts much more energetically than iodine trichloride.

J. R.

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## Action of Bromine on Aromatic Substances.

By E. Gessner (Deut. Chem. Ges. Ber., ix, 1049).

Benzene, when heated to 360°—400° with bromine containing iodine is converted into perbromobenzene. This body closely resembles perchlorobenzene, but it is much less soluble and melts only above 300°. It is formed by the ultimate action of bromine on toluene, phenol, and azobenzene. Naphthalene and diphenylamine, under the same circumstances, yield hexbromo- and decabromo-derivatives.

J. R.

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## Replacement of Bromine in the three Bromobenzyl Bromides.

By C. L. JACKSON (Deut. Chem. Ges. Ber., ix, 931—935).

IN this paper the author first describes more fully than he has done before the preparation and properties of the three isomeric bromobenzyl bromides ($C_6H_4Br.CH_2Br$) obtained by himself and Lowery.

*Parabromobenzyl bromide* is obtained by boiling the mixture of para- and ortho-bromotoluene formed by the action of bromine on toluene in the cold, and passing into the boiling liquid the vapour of an equal weight of bromine. The product is purified by distillation with steam. It crystallises from alcohol in needles, having an agreeable aromatic taste and melting at 61°. The vapour attacks the eyes, nose, and throat. The substance sublimes in needles and burns with a smoky, green-bordered flame. It is violently attacked by a mixture of potassium bichromate and sulphuric acid, and yields an acid melting at 239°—240°.

*Metabromobenzyl bromide* is formed by passing the vapour of bromine into boiling metabromotoluene prepared by Wroblevsky's method. The yield is very small. It crystallises in white needles, of an agreeable odour distinct from that of the para-compound. It melts at 41°. Volatilises very easily in ether-vapour. By oxidation with chromic acid it yields an acid which crystallises in needles and melts at 151°.

*Orthobromobenzyl bromide* is obtained by passing the vapour of bromine into boiling orthobromotoluene. In this case the bromine is absorbed much less readily than in either of the previous cases. The product could not be fully purified, owing to partial decomposition during distillation. It forms a colourless oil, which does not solidify at − 15°. The vapour, like that of the preceding compounds, attacks the mucous membranes. It is not affected by a mixture of potassium bichromate and sulphuric acid.

In order to estimate the relative facilities with which the bromine in the lateral chain of these three isomerides can be replaced, the author heated in a water-bath three small flasks containing a mixture of 4 grams of each of the three bromides with 2 grams of sodium acetate and 20 c.c. of absolute alcohol. After about half an hour the flasks were allowed to cool, and the amount of sodium bromide which had formed in each was estimated by precipitation with silver-nitrate. It was thus found that the amounts of bromine eliminated from 4 grams of the para-, meta, and ortho-compounds were 0·3927, 0·2884, and 0·0907 grams respectively, which numbers are in the ratio of 1 : 3·179 : 4·329. The square roots of these latter numbers are—

$$1, \qquad 1{\cdot}783, \qquad 2{\cdot}081.$$

Now if in a regular hexagon four consecutive angles be distinguished by the letters *a*, *b*, *c*. *d*, the lengths of straight lines joining the angles *a* and *b*, *a* and *c*, and *a* and *d* respectively are in the ratio of

$$1 \;:\; 1{\cdot}732 \;:\; 2.$$

The author thinks that the striking coincidence of these two series of numbers (due allowance being made for unavoidable errors of experiment) gives some support to the hypothesis that the differences in

the facility of replacement depend upon the distance between the bromine-atoms in the molecule, and that the amount of replacement increases with the square of this distance.

J. R.

## Dinitroparadibromobenzenes and their Derivatives.

By P. T. AUSTEN (Deut. Chem. Ges. Ber., ix, 918—921).

THIS is a continuation of a former paper on the same subject.

*β-Dinitroparadibromobenzene*, $C_6H_2Br_2(NO_2)_2$, is the chief product of the action of nitric acid on paradibromobenzene. It crystallises from its solution in carbon bisulphide in curved, thick needles, which are very soluble in glacial acetic acid, ethyl acetate, alcohol, &c. It melts to a yellow liquid at 99°—100°, and is partially volatilisable. The vapour, when inhaled, produces violent inflammation of the mucous membrane. An alcoholic solution causes painful inflammation and subsequent peeling of the skin.

*β-Dinitroparabromaniline*, $C_6H_2Br(NO_2)_2NH_2$, is formed when the preceding compound is heated to 100° with alcoholic ammonia in sealed tubes. It crystallises from alcohol in orange-red scales, which melt at 160°. It is easily soluble in boiling alcohol and glacial acetic acid, insoluble in boiling water and carbon bisulphide. When boiled with alcoholic potash it evolves ammonia and appears to be completely decomposed.

*β-Dinitroparabromanilidobenzene*, $C_6H_2Br(NO_2)_2NH.C_6H_5$, is formed by heating β-dinitroparadibromobenzene with aniline, when a violent reaction takes place. It crystallises from alcohol in orange-red, hair-like needles, which melt at 120°.

*β-Dinitroparabromonitranilidobenzene*, $C_6H_2Br(NO_2)_2NH.C_6H_4NO_2$, is formed by adding the preceding compound in small quantities to fuming nitric acid at 12°, and pouring the resulting solution into cold water. The bright-yellow powder which then separates crystallises from boiling glacial acetic acid in small brownish-yellow scales, which melt at 157·5°. When warmed with soda-ley it forms a blood-red solution, which quickly deposits dichroic red and green needles of a compound still under investigation.

J. R.

## Some Derivatives of Isoxylene.

By CH. GUNDELACH (Bull. Soc. Chim. [2], xxvi, 43—45).

XYLENE from coal tar was repeatedly fractionated by distillation so as to obtain a portion boiling at 137°—141°. The isoxylene thus obtained always contains some paraxylene, which is removed by oxidising, preferably with dilute nitric acid (1 : 3), with which it is boiled for 24 hours in a retort with inverted condenser. It is then distilled, the hydrocarbon treated with dilute ammonia, and again rectified, the portion passing over at 139° being collected.

*Remarks on Isotolyl Chloride.*—The chloride of isotolyl prepared from pure isoxylene boils at a rather higher temperature than that upon

which experiments have been made heretofore, since this latter has usually contained paraxylene.

*Isotoluic aldehyde* is produced, as indicated by Grimaux and Lauth (*Bull. Soc. Chim.*, xxv, 397), by treating isotolyl chloride, which need not be perfectly pure, so only that it be free from bichlorides, with lead nitrate, in the proportions of one part of isotyl chloride, half of lead nitrate, and seven of water, the mixture being boiled for 24 hours in a retort with inverted condenser, and then distilled.

The aldehyde passes over with the vapour of the water; the distillate is saturated with common salt in order to facilitate the separation of the aldehyde.

The isotolylic aldehyde is a colourless liquid smelling strongly of bitter almonds, boiling at 199°; combining with alkaline bisulphites, and reducing silver salts. It is nearly insoluble in water, soluble in alcohol and ether. It rapidly absorbs oxygen from the air, yielding isophtalic acid. The directions of several other reactions are noted, but they have not yet been fully investigated.

C. H. P.

**Retene and some of its Derivatives.** By A. G. EKSTRAND (Deut. Chem. Ges. Ber., ix, 855).

As regards the properties of retene (extracted from the so-called tar-tallow of a wood-tar oil factory), the results agree with those of Wahlfors. The formula is $C_{18}H_{18}$, and the melting point 98·5°. Substitution-products with chlorine were obtained with difficulty, owing to the quantity of resinous and syrupy products formed. Bromo compounds were obtained more easily, especially a dibromoretene and a tetrabromoretene, melting at 210°. The addition-products, as the dibromotetrabromide, $C_{18}H_{16}Br_2Br_4$, are decomposed by alcoholic potash. A mixture of Nordhausen and ordinary sulphuric acid forms the disulpho-acid, and probably, on heating, the trisulpho-acid. A particular object of the investigation was the product of oxidation with chromic acid—the so-called *dioxyretistene*, $C_{16}H_{14}O_2$, of Wahlfors. The products of decomposition of this body obtained by heating it with barium hydrate, $C_{22}H_{21}O$ (solid, crystalline), and $C_{21}H_{23}$ (liquid), are accounted for by the supposition of a previous polymerisation—$3C_{16}H_{14}O_2 = 2C_{24}H_{21}O_3$. No retistene, $C_{16}H_{14}$, could be obtained by heating with zinc-dust. The solid bodies obtained in small quantity proved to be a mixture of retene and dibenzyl, $C_{14}H_{14}$, with melting point 51°—52°. Two acids were extracted by caustic soda from the mixture of products of oxidation, on preparing dioxyretistene, viz., $C_{19}H_{16}O_3$, and $C_{18}H_{17}O_2$ (?), the former melting at 139°, the latter at 222°.

G. T. A.

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**Researches on the Turpentine Oils and Camphors.** By V. MEYER and F. V. SPITZER, No. 1 (Deut. Chem. Ges. Ber., ix, 877—880).

ALTHOUGH substitution-products of turpentine oil cannot be formed in the direct way—by the replacement of the hydrogen atoms by a

halogen element—yet Pfaundler, by the action of phosphorus pentachloride upon camphor, obtained a body, $C_{10}H_{15}Cl$, which there is reason for regarding as a chlorine substitution-product of terpene. This substance can be prepared with the greatest ease, and in almost the theoretical quantity, according to the following equation :—

$$C_{10}H_{16}O + PCl_5 = POCl_3 + HCl + C_{10}H_{15}Cl.$$

Its relation to terpene may be thus shown :—

| $C_{10}H_{14}$ | $C_{10}H_{14}\left\{\begin{matrix}H\\H\end{matrix}\right.$ | $C_{10}H_{14}\left\{\begin{matrix}H\\Cl\end{matrix}\right.$ |
|---|---|---|
| Cymene. | Terpene. | Monochloroterpene. (Pfaundler's chloride). |

The replacement of the chlorine in this compound by ethyl is very easy, but the attempt to substitute methyl has not yet succeeded.

*Eterpene* or *Ethylterpene*, $C_{10}H_{15}-C_2H_5$.—Pfaundler's chloride and ethyl iodide in the proportion of 1 molecule of the former to $1\frac{1}{2}$ of the latter, were dissolved in pure benzene, and some pieces of sodium added. The mixture was placed in a flask connected with a condenser, arranged so that the distillate should flow back into the flask, and the upper end of the condenser was closed by a tube dipping 330 m.m. into mercury. The flask was then heated over a water-bath, and after 16 hours' boiling, it was found that the sodium had disappeared, and a dark coloured crystalline mass was left in the flask. The benzene solution was now filtered off and distilled, when a considerable quantity of an oil remained behind in the retort. This oil, dried over calcium chloride, boiled at 140°—210°, and yielded, after repeated fractional distillation, a product boiling between 145° and 160°, which deposited a rich crop of crystals on cooling with ice. The mass of crystals was well pressed, once more distilled, and finally recrystallised from ether. It was the pure hydrocarbon, $C_{10}H_{15}-C_2H_5$, which the author proposed to name *eterpene* (Aeterpen), an abbreviation of *ethylterpene*.

The analysis of this substance gave :—

| | Calculated. | | Found. |
|---|---|---|---|
| $C_{12}$ ..... | 87·80 | ..... | 87·47 |
| $H_{20}$ ..... | 12·20 | ..... | 12·26 |
| | 100·00 | | 99·73 |

The reaction was, therefore, according to the equation :—

$$C_{10}H_{15}Cl + C_2H_5I + Na_2 = NaCl + NaI + C_{10}H_{15}-C_2H_5.$$

The oil boiling at the higher temperature, which smells like cymene, has not yet been examined.

Eterpene forms a dazzling-white crystalline mass, very similar, both in appearance and smell, to camphor, but of a different consistence, corresponding somewhat to that of wax. Its melting point is 63·5°. and it boils undecomposed at 153° (subject to future correction). It is insoluble in water, but dissolves freely in ether, benzene, &c.

H. H. B. S.

**Action of Chlorine on Nitronaphthalene.** By A. ATTERBERG (Deut. Chem. Ges. Ber. ix, 926—928).

IN a former paper the author described several bodies formed by the action of chlorine on nitronaphthalene (see this Journal, 1876, i, 915). He has since succeeded in obtaining from the portion of the crude product boiling above 305° a second *trichloronaphthalene*, which melts at 90°, and crystallises from alcohol in long shining needles.

The monochloronaphthalene described in the former paper is, the author now finds, identical with the liquid monochloronaphthalene obtained by other methods. From this substance and the new dichloronaphthalene (now called γ-dichloronaphthalene) previously described, the following bodies have been obtained by the action of nitric acid.

*Mononitrochloronaphthalene*, $C_{10}H_6ClNO_2$, crystallises from alcohol in bright yellow needles melting at 85°. This body, when treated with tin and hydrochloric acid, yields an amine having the properties of α-naphthylamine.

*α-Dinitrochloronaphthalene*, $C_{10}H_5Cl(NO_2)_2$, crystallises in long yellow soft needles, which melt at 106°, and dissolve easily in alcohol.

*β-Dinitrochloronaphthalene* crystallises from glacial acetic acid in pale-yellow brittle needles, which melt at 180°.

*Nitro-γ-dichloronaphthalene*, $C_{10}H_5Cl_2NO_2$, crystallises from glacial acetic acid and ethyl acetate in sulphur-yellow prisms, which dissolve sparingly in alcohol. It melts at 142°.

J. R.

**Substitution-products of Hydrocœrulignone.** By M. HAYDUCK (Deut. Chem. Ges. Ber., ix, 928—930).

*Dichloracetylhydrocœrulignone*, $C_{12}H_2Cl_2(OCH_3)_4(OC_2H_3O)_2$, is obtained by triturating diacetylhydrocœrulignone with an equal weight of phosphorus pentachloride, and warming the mixture for a few minutes. It crystallises in small colourless prisms, which melt at 172°.

*Dichlorohydrocœrulignone*, $C_{12}H_2Cl_2(OCH_3)_4(OH)_2$.—Diacetylhydrocœrulignone dissolves in alcoholic potash when boiled with it, but on continuing the boiling, the solution deposits an abundant precipitate, from the aqueous solution of which acids throw down a white gelatinous precipitate of dichlorhydrocœrulignone. This substance crystallises from hot alcohol in small colourless shining rhombic tables, which melt at 220°. Its *potassium-compound*, $C_{12}H_2Cl_2(OCH_3)_4(OK)_2$, is nearly insoluble in alcohol, and is, therefore, precipitated in the foregoing reaction: it dissolves easily in water, and crystallises from strong solutions in needles. The *barium-compound*, $C_{12}H_2Cl_2(OCH_3)_4O_2Ba$, is thrown down as a white amorphous precipitate on adding barium chloride to a solution of the potassium-compound. It acquires a yellow colour when heated.

*Dibromacetylhydrocœrulignone*, $C_{12}H_2Br_2(OCH_3)_4(OC_2H_3O)_2$, is formed by adding to a solution of acetylhydrocœrulignone in glacial acetic acid, the necessary quantity of bromine, precipitating with water, and crystallising the product from alcohol. It forms colourless needles, melting at 178°.

*Dibromhydrocœrulignone*, $C_{12}H_2Br_2(OCH_3)_4(OH)_2$, is obtained by boiling the preceding compound with alcoholic potash, decomposing with hydrochloric acid the sparingly soluble potassium-compound thereby precipitated, and crystallising the product from boiling alcohol or benzene. It forms distinct prisms melting at 262°.

*Tetrabromhydrocœrulignone*, $C_{12}Br_4(OCH_3)_4(OH)_2$, is formed in the same manner as the foregoing compound, an excess of bromine being employed. It crystallises in silky needles melting at 217—218°.

J. R.

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## On Anthraflavone and Anthraxanthic Acid.

By A. ROSENSTIEHL (Deut. Chem. Ges. Ber., ix, 946).

CRUDE anthraflavone is separable into two products, which behave differently towards bases:—

| *α-Anthraflavone.* | *β-Anthraflavone.* |
|---|---|
| The sodium-compound is very freely soluble in water, yielding a red solution. | The sodium-compound is sparingly soluble, especially in excess of soda. It crystallises in brilliant red needles, the solution of which is inclined to yellow. |
| Dissolves easily in baryta-water with red colour. | Dissolves in baryta-water only when boiling. The compound separates in red needles on cooling. |
| In alkaline solutions combines for the most part with alumina. | Does not combine with alumina, but remains in solution. |
| Is easily and completely converted into an isomeride of purpurin when heated to 130—135° with potash in close vessels. | Remains unaltered at 130—135°, oxidation first commencing at 200—205°. On this behaviour is based a method of purifying β-anthraflavone. |

J. R.

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## Preliminary Notice on the Action of Sulphuric Acid on Naphthalene.

By J. STENHOUSE and C. E. GROVES (Chem. News, xxxii, 151).

MERZ and Weith, in their researches on the naphthalene-sulphonic acids, found that when naphthalene in excess was heated with sulphuric acid at 180°, the product, besides *unaltered naphthalene*, consisted almost entirely of β-naphthalene-sulphonic acid. On repeating the experiment, however, the authors found that this supposed "unaltered naphthalene" contained a comparatively large quantity of sulphur-compound, and they succeeded in isolating therefrom three distinct crystalline substances. They find that the best method of obtaining satisfactory results is to heat a mixture of 8 parts of pure naphthalene with 3 of sulphuric acid at 180°; after a time a reaction sets in which continues for an hour or two, accompanied by the elimination of a considerable quantity of water. When water ceases to come over, the retort is

allowed to cool to about 100°, and water is added. The product, when quite cold, will be found to consist of two layers, the lower, a pasty crystalline mass of the β-sulphonic acid, the upper, a solid cake of a brownish-yellow colour. This cake consists of the new sulphur compounds mixed with excess of naphthalene, the latter of which may be removed by distillation in a current of steam. The sulphur-compounds, which consist of α- and β-naphthalene-sulphone, $C_{20}H_{14}SO_2$, and a third substance very soluble in carbon bisulphide, are separated by fractional crystallisation. The *α-naphthalene-sulphone* crystallises from carbon bisulphide in colourless transparent oblique prisms, which melt at 123°. It is insoluble in water, moderately soluble in boiling alcohol, and very soluble in hot benzene. Heated with concentrated sulphuric acid it dissolves, forming a sulphonic acid. The isomeric *β-naphthalene-sulphone* forms colourless silky needles melting at 177°, It is far less soluble than the β-sulphone, being dissolved with difficulty by carbon bisulphide or boiling alcohol; it is, however, moderately soluble in hot benzene or glacial acetic acid. It dissolves in hot concentrated sulphuric acid, forming a sulphonic acid. The authors have also obtained crystalline nitro-derivatives of both sulphones, which, in their turn, yield amido-compounds. An acetic acid solution of chromic anhydride oxidises the sulphones, converting them into crystalline compounds of a pale yellow colour.

C. E. G.

**Decomposition of Naphthalene Tetrachloride.** By F. KRAFFT and F. BECKER (Deut. Chem. Ges. Ber., ix, 1088—1090).

NAPHTHALENE tetrachloride, when decomposed by alcoholic potash, yields α-dichloronaphthalene melting at 35°—36°, as previously stated by Faust and Saame.

But when the tetrachloride is rapidly heated in small quantities and kept boiling for a short time, it is converted into β-dichloronaphthalene melting at 68° and boiling at 286°—287°.

When, however, the tetrachloride in larger quantity is boiled in a retort till hydrogen chloride is no longer evolved, the product consists of a mixture of α- and β-dichloronaphthalene.

J. R.

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**New Synthesis of Alizarin.—Constitution of Rufigallic Acid.** By O. WIDMAN (Deut. Chem. Ges. Ber., ix, 856).

JAFFÉ obtained anthracene from rufigallic acid by reduction with zinc dust, and therefore regarded the acid as hexoxyanthraquinone (*Berichte*, iii, 694), whilst Schiff, on the other hand (*Berichte*, iv, 968), regarded it, for other reasons, as the anhydride of digallic acid. If the first supposition were correct, a reduction going to a much less extent might lead to one of the anthraquinones poorer in oxygen. Other methods of reduction gave no result, but sodium amalgam produced, among other bodies, alizarin. Jaffé's formula would thus be supported. Unless some other method of reduction can be found, the discovery is, of course, useless for manufacturing purposes.

G. T. A.

**Nitroalizarin.** By A. ROSENSTIEHL (Compt. rend., lxxxii, 1455—1458).

SOME time ago, Strobel observed that by exposing madder-red to nitric acid, an orange colour was obtained which is not attacked by hot water or soap-solution, and is the brighter in colour the smaller the quantity of purpurin contained in the red dye from which it was derived. The new colouring matter is so slowly acted upon by acids, that the fibres of materials dyed therewith are destroyed before the colour can be removed. The orange dye is obtained by pouring a small quantity of alizarin-paste (No. I Meister, Lucius, and Co.) into a flask, spreading it out on the surface in a thin layer, and evaporating to dryness, after which nitric fumes are introduced into the flask. The flask is then corked up. In a few minutes the alizarin changes, and the vapours become decolorised. The contents are now treated with water, and the residue, which partly consists of unaltered alizarin (colouring alumina mordants red) and of the new substance (colouring mordants orange), is converted into the soda salt, which is much less soluble in water containing a slight excess of alkali. The colouring matter was then liberated by an acid and purified by a series of recrystallisations from chloroform. The dry product gave numbers corresponding with the composition of mononitroalizarin, $C_{14}H_7(NO_2)O_4$:

| | | Found. | Calculated. |
|---|---|---|---|
| C | = | 58·87 | 58·94 |
| H | = | 2·56 | 2·45 |
| N | = | 4·87 | 4·91 |

It is but little soluble in hot water, soluble in different neutral solvents, in acetic acid, and in sulphuric acid. When sublimed, it is partly destroyed, partly forms yellow, shining crystals, while at the same time red needles, similar to alizarin needles, are formed. Its alkaline solution has a reddish-violet colour. It saturates mordants in distilled water; the addition of one equivalent of calcium acetate somewhat increases the yield; the bicarbonate of the same metal totally precipitates the colour from the bath. The precipitation is retarded by a current of carbonic acid gas, which does not decompose the lime lake once formed. This property is used by the author for determining the presence of alizarin in the crude product. To oxides it does not behave like alizarin, but is similar to purpurin which, like it, is a tri-substitution derivative of anthraquinone. Its combinations with bases are distinguished by their relatively greater stability.

By reducing nitroalizarin two products are obtained, the one soluble in alkali with a blue colour, and dyeing mordants red, while the other colours alkaline mordants brown and dyes alumina mordants catechu-colour.

D. B.

## On a new class of Colouring Matters. By C. H. LAUTH (Compt. rend., lxxxii, 1441—1444).

THE raw materials for forming these new products are the aromatic diamines obtained by reducing the nitro-derivatives of the acetyl-compounds of organic bases. We take aniline, for example, prepare acetanilide, then nitroacetanilide and nitraniline, and reduce the nitraniline either with iron and acetic acid or with tin and hydrochloric acid. In the former case, an excess of lime is added, and then the liquid is distilled, whereby *β-phenylenediamine* is obtained in a pure state; in the latter, the tin is eliminated with zinc, whereby a mixture is obtained which may be directly used for the production of the colouring matter. The aniline brown obtained by the action of nitric acid on *α-phenylenediamine*, is the only substance of this class hitherto produced that is of any interest with regard to the production of dyes; but by introducing into β-phenylenediamine a new element, namely, sulphur, different results are obtained. *Thio-β-phenylenediamine* is probably obtained when the diamine is heated with its own weight of sulphur at 150—180°. After the reaction, which is accompanied by the elimination of much sulphuretted hydrogen, has terminated, the residue is taken up with hot hydrochloric acid and filtered, in order to separate the excess of sulphur. The filtrate obtained gives, with oxidising agents, splendid violet and blue colours. It is, perhaps, more advantageous to effect the sulphuration and oxidation in one process. To this effect we saturate the hydrochloric acid solution of the phenylenediamine (utilising the above-mentioned liquor containing the zinc) with sulphuretted hydrogen, and add ferric chloride. The sulphur set free combines in the nascent state with the base, and by gradually adding the oxidising agent, the colouring matter will develop itself and be precipitated. After filtration, the impurities are removed by washing with water, and dissolving the residue in hot water; if the liquid is then left to cool, a pure and magnificently crystallised product is obtained. For 20 *grams* of the *phenylenediamine chlorhydrate* the author uses—

| | |
|---|---|
| Sulphuretted hydrogen water ..... | 4000 c.c. |
| Hydrochloric acid ..... | 20 grams |
| Ferric chloride (1 in 10 solution) ..... | 500 c.c. |

This new violet colour surpasses the *violets de Paris*. In its dry state it has a dark greenish-brown colour, and readily crystallises in long silky fibres. It is very soluble in pure water, but the smallest quantity of foreign matter modifies its solubility. If soda be added to the violet solution, a brown precipitate is obtained, which certainly forms the base of the new colour. Acids precipitate the solution, but an excess of acid redissolves the precipitate. Acetic acid forms a violet, mineral acids a pure blue solution. Metallic salts give a violet precipitate, which redissolves when the salt has been eliminated by washing. Zinc chloride gives a very bulky violet precipitate; sodium chloride separates the violet from its solution, but transforms it partly into a new violet substance, insoluble in water. If this precipitation be repeated several times, a complete transformation will be the result,

the soluble colouring matter disappearing entirely. Tannin forms, with the violet, a compound insoluble in water. Reducing agents decolorise the new body, but mere agitation in contact with air will reproduce the primitive colour. Oxidizing agents destroy the colour very rapidly. The new colouring matter is capable of giving by substitution other colouring derivatives; if heated with aniline, it gives a blue insoluble in water and soluble in alcohol; if submitted to the action of aldehyde, methyl iodide, &c., under ordinary conditions, by it is transformed in a pure bluish-green; and in dyeing it is fixed by immersing the fibre into the bath, a property of some interest, as aniline colours require much care and skill in dyeing. In conclusion, the author mentions that sulphur plays a great part in the constitution of colouring matters, and as we may suppose other simple bodies to have analogous properties, the field of research for the production of artificial colours, which was at one time limited to a small number of reactions, is now greatly extended. What part does the sulphur occupy in the constitution of these new substances? Does it enter the phenol nucleus, or does it, on the contrary, link together a certain number of groups by its polyatomicity? Or is there a relation between the introduction of sulphur and the existence of diatomic radicles in these substances? These are questions which future researches will, no doubt, explain.

D. B.

**Synthesis of Polybasic Acids by means of Salicylic Acid and Carbon Dioxide.** By H. Ost (J. pr. Chem. [2], xiv, 93—124).

In a former paper the author showed that salicylic acid, when heated with caustic potash, readily yields oxybenzoic acid, but that when caustic soda is substituted for potash no oxybenzoic is formed (see this Journal, 1876, i, 252). The present paper gives the results of further experiments on the same subject.

When basic sodium salicylate is heated to between 300° and 400° in a current of carbon dioxide, the salicylic acid disappears, partially or entirely, and in its place two new acids are found, the composition of which agrees with the formulæ $C_6H_3(OH)(COOH)_2$ and $C_6H_2(OH)(COOH)_3$ respectively. These acids are called by the author *orthophenoldicarbonic* and *orthophenoltricarbonic acids*. They are formed from salicylic acid by a reaction which is analogous to, or rather a continuation of, that by which salicylic acid itself is formed when sodium phenol is heated in a current of carbon dioxide. Comparative experiments have shown that the reaction proceeds most rapidly at 370—380°, at which temperature salicylic acid is, in the course of a few hours, completely converted into the di- and tricarbonic acids, the latter always preponderating. The new acids are insoluble in chloroform, and by means of it are easily separated from unaltered salicylic acid.

*Orthophenoldicarbonic acid*, $C_6H_3(OH)(COOH)_2$, when pure, crystallises in needles, which dissolve easily in alcohol and ether, and in 5,000 parts of water at 10°. In general appearance, it closely re-

sembles salicylic acid. It produces an intense reddish-violet coloration with ferric chloride. It melts at 270—280°, and sublimes with partial decomposition. The acid is a di-basic oxyacid, and is, therefore, capable of forming three series of salts, neutral, acid, and so-called basic salts, that is, salts in which the hydrogen of the hydroxyl-group in phenol is replaced by metals. The neutral salts are formed by neutralising the acid with carbonates.

The *sodium salt*, $C_6H_3(OH)(COONa)_2$ + aq., crystallises in long needles, which retain 2 mols. of water when dried in the air, and dissolve easily in water. The *potassium*, *ammonium*, *barium*, *calcium*, *zinc*, *manganese*, *cobalt*, *nickel*, and *cadmium salts* are all soluble in water. The sodium salt, when heated to 220—250°, undergoes decomposition in the same manner as neutral sodium salicylate, yielding the basic salt, phenol, and carbon dioxide:

$$3[C_6H_3(OH)(COONa)_2]=2[C_6H_3(ONa)(COONa)_2]+C_6H_5OH+2CO_2.$$

The *neutral silver salt*, $C_6H_3(OH)(COOAg)_2$, obtained by precipitating the ammonium salt with silver nitrate, is amorphous and nearly insoluble in water.

The *acid silver salt*, $C_6H_3(OH)COOH.COOAg$, is formed by adding to the free acid an excess of silver nitrate. It crystallises in needles, which dissolve in water.

The *basic calcium salt*, $\begin{matrix}C_6H_3O\\C_6H_3O\end{matrix}Ca\left(\begin{matrix}COO\\COO\end{matrix}Ca\right)_2 + 5H_2O$, obtained by adding lime-water to a solution of the neutral salt, is sparingly soluble in water.

*Ethyl phenoldicarbonate*, $C_6H_3(OH)(COOC_2H_5)_2$, is obtained by passing hydrogen chloride into an alcoholic solution of the acid. It distils with steam in snow-white crystals, which melt at 52°.

*Orthophenoltricarbonic acid*, $C_6H_2(OH)(COOH)_3$, crystallises from alcohol in needles, and from water in prisms containing 1 mol. or needles containing 2 mols. of water. It dissolves freely in alcohol, sparingly in ether, and in 200 parts of water at 10°. It produces an intense deep-red coloration with ferric chloride. When heated it undergoes complete decomposition, yielding chiefly phenoldicarbonic acid and carbon dioxide, with a little salicylic acid and phenol. It is a tribasic acid, and is capable (since it contains the hydroxyl-group of phenol) of forming four series of salts. The neutral salts of the alkalis are crystallisable and easily soluble in water. All others are either insoluble or but sparingly soluble.

The *neutral barium salt*, $[C_6H_2(OH)(COO)_3]_2Ba_3 + 8H_2O$, and the corresponding *calcium salt*, obtained by double decomposition, are very sparingly soluble in water.

The *neutral silver salt*, $C_6H_3(OH)(COOAg)_3 + 3H_2O$, is a crystalline precipitate.

The *di-acid calcium salt*, $[C_6H_2(OH)(COOH)_2COO]_2Ca + 6H_2O$, and the corresponding barium salt, are formed by mixing solutions of the free acid with calcium or barium chloride. They are crystalline and soluble in water.

Acid salts of other metals and ammonia have also been prepared.

*Ethyl phenoltricarbonate*, $C_6H_2(OH)(COOC_2H_5)_3$, is readily formed by passing hydrogen chloride into an alcoholic solution of the acid. It crystallises from a hot alcoholic solution in long colourless prisms, which melt at 84° and sublime with partial decomposition at a higher temperature. When boiled with aqueous soda it is slowly decomposed, yielding phenoltricarbonic acid, but when it is digested with soda in the cold the hydrogen of the hydroxyl-group is replaced by sodium, whereby the following compound is formed.

*Ethyl sodium-phenoltricarbonate*, $C_6H_2(ONa)(COOC_2H_5)_3$. This body is best obtained by dissolving the foregoing ether in absolute alcohol and adding alcoholic soda, whereupon it crystallises in large oblique prisms. It is insoluble in water, cold alcohol, and ether. When boiled with water for some time it gradually dissolves, forming a solution which on cooling deposits needles of—

*Sodium diethylphenoltricarbonate*, $C_6H_2(OH)(COOC_2H_5)_2COONa$. This substance crystallises from alcohol with 1 mol. of water. Its aqueous solution, which is neutral, gives precipitates with salts of barium, silver, and other metals.

*Diethylphenoltricarbonic acid*, $C_6H_2(OH)(COOC_2H_5)_2COOH$, is precipitated on saturating an aqueous solution of the foregoing salt with hydrogen chloride. It crystallises from alcohol in long needles containing 1 mol. of water. The anhydrous substance melts at 118°.

J. R.

**Action of Nitric Acid on Oxyuvitic Acid.** By O. EMMERLING and A. OPPENHEIM (Deut. Chem. Ges. Ber., ix, 1094—1096).

OXYUVITIC yields by oxidation with dilute nitric acid the same hydroxybenzoic acid as is formed by other oxidising agents. Strong nitric acid also forms the same substance, together with a nitro-product. Fuming nitric acid, especially when mixed with sulphuric acid, converts oxyuvitic acid into *trinitrocresol*, $C_6H.CH_3.OH.(NO_2)_3$, which crystallises when pure in yellowish needles melting at 106°. It forms an orange-red potassium salt, which is much more soluble than potassium picrate.

An alcoholic solution of trinitrocresol, when treated with hydrogen sulphide, yields *dinitro-amidocresol*, $C_6H.CH_3.OH.NH_2(NO_2)_2$. This substance crystallises in brilliant amber-yellow needles, which melt at 156° and decompose at a somewhat higher temperature. It is soluble in alkalis but not in acids. Its alcoholic solution, when treated with nitrous acid, yields golden laminæ of *dinitrodiazo-amidodinitrocresol*—

$$C_6H(CH_3)(OH)(NO_2)_2N{=}N{-}NH.C_6H.CH_3.OH(NO_2)_2,$$

which explodes violently at 160°.

J. R.

**Derivatives of Dimethylprotocatechuic and Vanillic Acids.** By F. TIEMANN and U. MATSMOTO (Deut. Chem. Ges. Ber., ix, 937—945).

THE dimethylprotocatechuic acid from which the following derivatives were prepared was obtained by the oxidation of methyleugenol as follows:—One part of methyleugenol was agitated with 10—15 parts of water at 80—90°, and into the emulsion thus formed a solution of 3½ parts of potassium permanganate at 80—90° was introduced with constant stirring. After the manganic hydrate thereby formed had settled, the supernatant colourless liquid was filtered and evaporated to a small bulk, and the dimethylprotocatechuic acid contained in it was precipitated by hydrochloric acid and purified by crystallisation from boiling water.

Dimethylprotocatechuic acid when treated with nitric acid yields a nitrated acid, together with indifferent products insoluble in ammonia, the proportion of the latter being greater the stronger the acid and the more prolonged its action.

*Nitrodimethylprotocatechuic acid*, $C_6H_2(NO_2)(OCH_3)_2COOH$, is obtained by warming dry dimethylprotocatechuic acid with nitric acid of sp. gr. 1·25 till the first violent action is over. On addition of water a yellow flocculent mass is thrown down, from which the acid is extracted by ammonia, indifferent products remaining undissolved. The acid, when pure, crystallises in yellow needles containing ½ mol. of water, easily soluble in alcohol, ether, and hot water. The *ammonium salt*, $C_9H_8(NH_4)NO_6$, crystallises in pale-yellow needles, easily soluble in water and sparingly in alcohol. It loses ammonia at 100°. The *silver salt*, $C_9H_8AgNO_6$, is a pale-yellow precipitate, which dissolves in boiling water and crystallises in fine pale-yellow needles. It is stable and does not blacken in the light. The *ethyl compound*, $C_9H_8(C_2H_5)NO_6$, is formed by saturating with dry hydrogen chloride a solution of the acid in absolute alcohol, distilling off excess of alcohol, and adding water, when the ethyl-compound is thrown down as a yellow oil, which afterwards solidifies. It crystallises from weak spirit in nacreous flat prisms, which melt at 99—100° and dissolve in alcohol and ether.

When a solution of nitrodimethylprotocatechuic acid in hot water is treated with tin and hydrochloric acid the liquid, on cooling, deposits crystals of a double-salt of *stannous chloride* and *amidodimethylprotocatechuic hydrochloride*—

$$C_6H_2(NH_2)\left\langle\begin{matrix}OCH_3\\OCH_3,HCl\\COOH\end{matrix}\right. + SnCl_2.$$

Amongst the indifferent bodies formed by the action of nitric acid on dimethylprotocatechuic acid are the following, which have been isolated and analysed:—

1. *Mononitrodimethylpyrocatechin*, $C_6H_3(NO_2)(OCH_3)_2$, crystallises in fine yellow needles, which melt at 95—96°, and dissolve sparingly in water, easily in alcohol and ether.

2. *Trinitrodimethylpyrocatechin*, $C_6H(NO_2)_3(OCH_3)_2$, crystallises in

white glistening prisms, which melt at 144°—145° and dissolve in hot alcohol and ether.

*Ethyl dimethylprotocatechuate*, $C_9H_9(C_2H_5)O_4$, is formed in the same manner as the corresponding nitro-compound. It crystallises in colourless needles melting at 43—44°, boiling at 295—296°, and dissolving in alcohol and ether.

*Nitracetovanillic acid*, $C_6H_2(NO_2)\left\langle\begin{matrix}OCH_3\\OC_2H_3O\\COOH\end{matrix}\right.$, is formed by the action of nitric acid on acetovanillic acid. It crystallises in colourless needles, which melt at 181—182° with partial decomposition.

*Nitrovanillic acid*, $C_6H_2(NO_2)\left\langle\begin{matrix}OCH_3\\OH\\COOH\end{matrix}\right.$.—This body cannot be obtained by the direct action of nitric acid on vanillic acid. It is formed, together with sodium acetate, by heating the preceding compound with dilute soda-ley. It forms white glistening needles, which decompose without melting at 210°. Its *sodium-salt* crystallises in yellow needles.

J. R.

## Naphthylphosphinic Acid. By W. Kelbe (Deut. Chem. Ges. Ber., ix, 1051).

This substance was obtained by heating mercury-diphenyl to 200° with phosphorus trichloride, when the following reaction took place:—

$$(C_{10}H_7)_2Hg + 2PCl_3 = 2C_{10}H_7PCl_2 + HgCl_2.$$

The naphthylphosphorous chloride thus formed was then treated with chlorine, and the resulting tetrachloride, $C_{10}H_7PCl_4$, decomposed with water.

Naphthylphosphinic acid, $C_{10}H_7PO(OH)_2$, crystallises in long needles, which dissolve in hot water and melt at 190°. When strongly heated it breaks up into naphthalene and metaphosphoric acid. The silver salt, $C_{10}H_7PO(AgO)_2$, is a white precipitate, blackening in the light; it dissolves in ammonia and nitric acid.

J. R.

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## Phosphenyl Sulphochloride and some Derivatives. By H. Kohler and A. Michaelis (Deut. Chem. Ges. Ber., ix, 1053—1054).

Phosphenyl chloride dissolves sulphur readily. On warming the solution it becomes dark-coloured and the two substances combine with violent ebullition, or when in larger quantities with incandescence. The product, when distilled, yields at 270° a colourless liquid having the composition of phosphenyl sulphochloride, $C_6H_5PSCl_2$. This body distils without decomposition under reduced pressure only: under 130 mm. it boils at 205°. Its sp. gr. at 13° is 1·376. In general properties it resembles phosphorus sulphochloride. It fumes in the

air and is decomposed by water on prolonged boiling, yielding phosphenylic acid—

$$C_6H_5PSCl_2 + 3H_2O = C_6H_5PO(OH)_2 + 2HCl + H_2S.$$

It is decomposed by potash in the same manner as phosphorus sulphochloride—

$$C_6H_5PSCl_2 + 4KHO = C_6H_5PS(OK)_2 + 2KCl + 2H_2O;$$

this reaction being accompanied, however, by another, of which the product is a hydrocarbon melting at 70°—probably diphenyl.

Phosphenyl sulphochloride dissolves in alcohol with rise of temperature, forming a solution from which water throws down the *ethyl-ether*, $C_6H_5PS(OC_2H_5)_2$. This is an oily body of faint aromatic odour, decomposing when distilled.

The sulphochloride likewise reacts with phenol to form the *phenyl-ether*, $C_6H_5PS(OC_6H_5)_2$, which is being investigated.

J. R.

**Benzhydroxamic Ether.** By MARTIN E. WALDSTEIN (Liebig's Annalen, clxxxi, 384—394).

THE ethylbenzhydroxamic acid of Eiseler (*Liebig's Annalen*, clxxv, 332; this Journal, xxviii, 766), may be represented by one of the following formulæ:—

$$N.H.(OC_2H_5)(C_7H_5O), \text{ or } N(C_2H_5).OH.(C_7H_5O),$$
$$\text{or } NH(C_2H_5).(OC_7H_5O).$$

For the purpose of deciding which of these truly represents the constitution of Eiseler's body, it was necessary to ascertain whether it was identical with, or merely isomeric with the compound to be obtained by acting with ethyl iodide on a salt of benzhydroxamic acid.

The action of ethyl iodide on lead benzhydroxamate proving too slow and imperfect, the potassium salt was made use of, and the resulting benzhydroxamic ether prepared in the following manner. Benzhydroxamic acid was dissolved in a concentrated alcoholic solution of potassium hydrate, in the proportion of one molecule of acid to two of the alkali, and an equivalent proportion of ethyl iodide added. After standing for 24 hours, the potassium iodide was removed by filtration, the filtrate evaporated to dryness, taken up with water, and a current of carbonic anhydride passed through the liquid. The benhydroxamic ether separated in oily drops which were taken up with common ether, dried, and freed from common ether by evaporation. Thus prepared, the crystalline mass was contaminated by a thick oil, from which it was freed by pressure between filter paper and recrystallisation from alcohol.

Benzhydroxamic ether forms white crystalline tables of considerable size, and belonging apparently to the rhombic system. It melts between 64° and 65°, possesses a feeble aromatic odour, is very easily soluble in ether and alcohol, slightly soluble in water. Like Eiseler's ethylbenzhydroxamic acid, it exhibits the properties of a feeble acid, and dissolves readily in alkaline solutions. It dissolves in fixed alkalis:

an experiment with a titrated solution of potassium hydrate showed that 1 mol. of the ether is dissolved by 1 mol. KHO. The solution is precipitated by salts of silver. It unites in molecular proportions with potassium hydrate, mercury, and lead.

On analysis benzhydroxamic ether gave numbers corresponding with the formulæ—

$$NH(OC_2H_5)(OC_7H_5O).$$

The action of very concentrated hydrochloric acid at high temperatures on benzhydroxamic ether was examined, and by this means glittering scaly needles were obtained, which on analysis proved to be ethylhydroxamine hydrochloride, $N(C_2H_5)H_2O.HCl$. This compound unites with platinum chloride to form orange-yellow crystalline needles of the formula $2[N(C_2H_5)H_2O.HCl] + PtCl_4$, which are easily soluble in water and alcohol. Eiseler's ethylbenzhydroxamic acid is readily decomposed by hydrochloric acid into benzoic ether and hydroxamine, an essentially distinct reaction.

The above reaction establishes the fact that Eiseler's ethylbenzhydroxamine acid and benzhydroxamic ether are distinct bodies, and not identical, so that the constitution of these two bodies must be—ethylbenzhydroxamic acid $= N(C_2H_5)OH.(C_7H_5O)$; benzhydroxamic ether $= NH(OC_2H_5)(C_7H_5O)$. It is moreover evident, from the existence of these two isomerides, that the structural formulæ of benzhydroxamine must be $NH.OH.(C_7H_5O)$, as the constitution $NH_2(OC_7H_5O)$ does not permit the existence of two isomeric ethyl-derivatives. The general constitution of the benzhydroxamates must be, therefore, $NH(OM)(C_7H_5O)$. Incidentally the above reactions also establish $NH_2(OC_2H_5)$ as the formulæ of ethylhydroxamine.

*Methylbenzhydroxamic ether*, $N(CH_3)(OC_2H_5)(C_7H_5O)$, was prepared by the action of methyl iodide on the silver compound of benzhydroxamic ether, the reaction being completed in a few hours. After dissolving in ether, the silver iodide was removed, and then the ether evaporated off. Methylbenzhydroxamic ether was thus obtained as an oily liquid with an aromatic odour, insoluble in water, but soluble in any proportion in alcohol and ether. By highly concentrated hydrochloric acid it is split up into ethylhydroxamine hydrochloride and methyl benzoate. E. N.

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## Aromatic Hydrazin-compounds. By Emil Fischer (Deut. Chem. Ges. Ber., ix, 880—891).*

Diazoamidobenzene and the diazobenzenediethylamide of Baeyer and Jaeger (*Deut. Chem. Ges. Ber.*, viii, 148), in alcoholic solution, are attacked by zinc-dust and acetic acid, yielding phenylhydrazin. In the case of diazoamidobenzene the reaction is as follows:—

$$C_6H_5.NNN.C_6H_5 + 4H = C_6H_5.NH—NH_2 + NH_2.C_6H_5.$$

It has been before shown that phenylhydrazin can be combined with carbon bisulphide to form a compound, $(C_6H_5.N_2H_3)_2CS_2$. This compound can be split up into phenylhydrazin, and a new body of the

* See also *Journ. Chem. Soc.*, 1875, 1034; 1876, vol. i, 576 and 713.

formula $C_6H_5.N_2H_2.CS.SH$, which the author names *phenylsulphocarbazic acid.* It is very unstable, and steadily decomposes even at the ordinary temperature; but on warming, carbon bisulphide, sulphuretted hydrogen, and ammonia gas are successively disengaged, and if, at this stage, the decomposition be arrested, and the residue be treated with hot alcohol, a body can be isolated of the composition $(C_6H_5N_2H_2)_2CS$, identical with that obtained by the action of heat upon phenylhydrazin phenylsulphocarbazate.

Phenylhydrazin and ethyl iodide react upon each other very energetically, gas being evolved with explosive violence, but if ethyl bromide be substituted for the iodide, the reaction proceeds more quietly. From the products of this reaction the author has isolated a body of the formula $C_6H_5.N_2H_2(C_2H_5)(C_2H_5Br)$, which he names *phenyldiethylhydrazoniumbromide.* It is easily soluble in water and hot alcohol; silver salts and silver oxide deprive it of its bromine, but alkalies have no action upon it.

Benzoic aldehyde and phenylhydrazin combine, forming the compound $C_6H_5.N_2H.CH.C_6H_5$, water being set free, thus:—

$$C_6H_5.N_2H_3 + C_6H_5\,COH = H_2O + C_6H_5.N_2H.CH.C_6H_5.$$

Acetic aldehyde acts in exactly the same manner upon phenylhydrazin, producing the compound $C_6H_5.N_2H.CH.CH_3$.

The action of 1 molecule of acetyl chloride, or acetic anhydride, upon 2 molecules of phenylhydrazin yields a monacetyl derivative, *phenylacetazide*, the analysis of which agrees with the formula $C_6H_5.N_2H_2(C_2H_3O)$.

H. H. B. S.

## Trinaphthylene-diamine. By M. Salzmann and H. Wichelhaus (Deut. Chem. Ges. Ber., ix, 1107).

This substance is formed in almost theoretical amount by heating to 190—220° in a sealed tube equal numbers of molecules of naphthylamine, nitronaphthalene, and naphthylamine hydrochloride. The crude product is purified by treating it with hot water to remove ammonium chloride, then adding potash, and exposing it to the action of superheated steam to expel traces of naphthylamine and nitronaphthalene, and finally dissolving it in alcohol and precipitating with water. The pure substance dried at 100° contains 1 mol. of water, which is expelled at 120—125°. Its composition then agrees with the formula $C_{30}H_{18}N_2$. The base forms an amorphous blue-black powder, soluble with red colour in alcohol, chloroform, and benzene. It begins to decompose at 180°. Its hydrochloride is an amorphous violet powder, more easily soluble than the base. As dyes, both the base and the salt produce reddish-violet colours, which, however, are not very good.

J. R.

**On Rosaniline.** By EMIL FISCHER and OTTO FISCHER (Deut. Chem. Ges. Ber., ix, 891—900).

DIAZOROSANILINE chloride (prepared by Griess's method), when mixed in aqueous solution with gold trichloride and hydrochloric acid, gives a bright yellow, flocculent-crystalline precipitate of a compound agreeing in composition with the formula $C_{20}H_{13}N_6Cl_3 + 3AuCl_3 + H_2O$. This compound is analogous in properties to the corresponding compound of diazobenzene. It explodes when heated, and when boiled with water it evolves the whole of its nitrogen in the gaseous form. A similar compound is formed with platinic chloride.

The composition of the gold-compound, the authors think, justifies them in assigning to diazorosaniline chloride the formula $C_{20}H_{13}(N_2Cl)_3$.

Rosaniline combines directly with hydrogen cyanide to form hydrocyanorosaniline, $C_{20}H_{20}(CN)N_3$, which behaves as an independent base. The diazo-compound of this body, formed by passing nitrous acid into its solution in hydrochloric acid, gives with gold trichloride a double salt of the formula $C_{20}H_{14}(CN)N_6Cl_3 + 3AuCl_3$. Its sulphate, when decomposed by water, yields a brown product consisting chiefly of hydrocyanorosolic acid, the formation of this product being perfectly analogous to the formation of rosolic acid from rosaniline.

From these data it follows that hydrocyanorosaniline is a triamine, having the formula $C_{20}H_{14}(CN)(NH_2)_3$, and is formed by the addition of the elements of hydrocyanic acid to the hydrocarbon residue in rosaniline. Assuming this addition to take place without molecular transposition, of which there is no evidence, rosaniline itself must contain three amido-groups, and hence its formula becomes $C_{20}H_{13}(NH_2)_3$. This the authors believe to be the true formula of rosaniline, notwithstanding the fact that they have not been able to obtain the corresponding hydrocarbon, $C_{20}H_{16}$, by decomposing the diazo-compound with alcohol. They have, however, succeeded in obtaining the hydrocarbon, $C_{20}H_{18}$, which they regard as the starting-point of the rosaniline group of bodies, by decomposing the diazo-compound of leucaniline with alcohol in the ordinary way.

Diazoleucaniline is formed by passing nitrous acid into a solution of the base in hydrochloric acid. Its chloride dissolves with characteristic greenish-blue colour in water, and is easily decomposed by boiling, when it deposits a dirty-brown precipitate, which is only partially soluble in potash. It combines with gold trichloride to form a compound having the formula $C_{20}H_{16}N_6Cl_3 + 3AuCl_3 + H_2O$. The diazo-compound in the free state dissolves sparingly in alcohol, and when warmed therewith is deposited for the most part in the form of a resin. To obtain the hydrocarbon mentioned above the authors proceed as follows:—A solution of leucaniline in strong sulphuric acid is treated with nitrous acid, freed from excess of the latter by means of a current of air, and added gradually to boiling alcohol. The liquid, after being neutralised, is evaporated to a small bulk, and then largely diluted with water, and the oil thereby separated is taken up with ether. This oil, after purification, has the composition indicated by the formula $C_{20}H_{18}$. It boils without decomposition considerably above 360°, and dissolves easily in ether and benzene, sparingly in alcohol

and wood-spirit. It crystallises with difficulty even when quite pure: the solid substance melts at 58°. When dissolved in glacial acetic acid it gives, with fuming nitric acid and with bromine, nitro- and bromo-derivatives, which crystallise with difficulty. By oxidation with chromic acid it yields a ketone, $C_{20}H_{16}O$, crystallising in colourless laminæ, which melt at 148°—149°. The constitution of the hydrocarbon remains to be investigated.

J. R.

**On Veratrine.** By ERNST SCHMIDT and RUD. KÖPPEN (Deut. Chem. Ges. Ber., ix, 1115—1121).

CRYSTALLISED veratrine was prepared by the authors, according to the directions of Merk, partly from commercial veratrine and partly from veratrine made by themselves. The general properties of the substance accord with the statements of Merk and Weigelin respecting it. It melts at 205°. The numbers obtained by analysis (64·63 p.c. carbon, 8·68 p.c. hydrogen, 2·66 p.c. nitrogen) lead to the formula $C_{32}H_{50}NO_9$. The hydrochloride forms with gold trichloride the compound $C_{32}H_{50}NO_9HCl + AuCl_3$, which crystallises in yellow needles; with platinum tetrachloride an indistinctly crystalline compound $(C_{32}H_{50}NO_9HCl)_2 + PtCl_4$; and with mercuric chloride a white crystalline precipitate, $C_{32}H_{50}NO_9HCl + HgCl_2$. The sulphate $(C_{32}H_{50}NO_9)_2 H_2SO_4$, and hydrochloride are non-crystallisable.

Crystallised veratrine is insoluble in water, but on prolonged washing therewith it becomes transformed into a soluble modification, the solution of which leaves when evaporated a yellowish amorphous mass having the same composition as the crystals. Veratrine dissolved in water is rendered insoluble, and is consequently precipitated, by heating the solution. Acids also appear to convert the soluble into the insoluble modification.

Several samples of commercial veratrine examined by the authors were found to be almost pure.

J. R.

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**Does Veratrum viride contain an Alkaloïd other than Jervine?** By CHARLES BULLOCK (Pharm. J. Trans. [3], vi, 1009).

THE portion of the alkaloïd taken up by ether gave, when dissolved in acetic acid, a copious precipitate on addition of potassium nitrate; this appeared to indicate the presence of jervine dissolved under some peculiar conditions. It was found on investigation that the so-called veratroidine is a mixture of jervine and a resin, the resin favouring by its presence the solution of the jervine in ether, and also producing a marked difference in the physiological effects of jervine. The author concludes that jervine is the only alkaloïd present, and he obtains it white by digesting the nitrate with sodium hydrate, washing, redissolving in acetic acid, precipitating again by soda, and recrystallising from alcohol. The crystals, which are prismatic, resemble morphine, are insoluble in ether, and melt at 380—385° F.

E. W. P.

**On Ergot of Rye.** By DRAGENDORFF (Pharm. J. Trans., [3], vi, 1001).

ON treating ergot with water, a colloïd substance is dissolved, which is precipitated by the addition of 40—45 p.c. alcohol. This substance (scleromucin) when once dried is soluble with difficultly in water, contains nitrogen, but gives no albuminoïd reaction. In ergot there also occurs a substance (sclerotic acid) soluble in 45 per cent. alcohol, which passes into the diffusate after dialysis, but is colloïdal after its separation in the pure state. It is precipitated by 90 per cent. alcohol, together with lime, &c., but after treatment with hydrochloric acid, may be separated from the ash by addition of alcohol. Calcium sclerotate leaves on combustion 19—20 per cent. of calcium carbonate. Sclerotic acid appears to be well adapted for therapeutic purposes by reason of its easy solubility in water, and that it does not alter the cellular tissue lying under the skin, whereas scleromucin, being only partially soluble in water, cannot be recommended.

Sclerotic acid gives no albuminoïd, alkaloïd, or glucosidal reactions; it is tasteless, scentless, colourless, and slightly hygroscopic.

The red colouring matter is dissolved by alcohol after ergot has been treated with an aqueous solution of tartaric acid; from this substance (sclererythrin), on further purification, a brown resinous mass separates. Sclererythrin is insoluble in water, but soluble in alcohol, ammonia-solution, &c.; its alkaline solutions are of a murexid colour: with aluminium sulphate and zinc chloride it forms a red mixture, and with barium salts, &c., it gives a blue precipitate. The amount of this body contained in ergot is very small, and it is supposed to stand in near relation to chrysophanic acid and alizarin. Together with sclererythrin another colouring matter is obtained, which when isolated is no longer soluble in water, &c., but dissolves in potash with a violet colour, from which it is precipitated by acetic acid; concentrated sulphuric acid dissolves it with a blue colour, and on this account it has been called *scleroïodin*; it is similar to sclererythrin, of which it is probably a decomposition-product.

After sclererythrin and scleroïodin have been removed from ergot powder, ether takes up a mass which crystallises partly in colourless needle crystals, partly in citron-yellow crystals. The needle crystals (sclerocrystallin) are almost insoluble in water, &c., but soluble in ammonia and potash solutions, and have the composition $C_{10}H_{10}O_4$. The yellow crystalline body (scleroxanthin) appears to be a hydrate of sclerocrystallin, and is represented by the formula, $2C_{10}H_{10}O_4 + 3H_2O$, for by heating it with chloroform, it is transformed into the latter substance. Neither of them has any effect on frogs. Two other substances have been found, but not examined. Ergotine and ecboline, which are inactive, are probably identical. Tanret's ergotinin, is supposed to be a mixture of sclererythrin with other substances.

E. W. P.

## Erythrophlœum guineense, and E. couminga.

By N. GALLOIS and E. HARDY (Bull. Soc. Chim. [2], xxvi, 39—42).

THE *Erythrophlœum guineense* is a tall tree belonging to the family *Leguminosæ*, and growing along the west coast of Africa. Its wood is very hard, and is covered with a hard fibrous and odourless bark, which contains an active poison, and to which the name of *erythrophleine* has been given. Erythrophleine is a base and may be obtained by extracting the pulverised bark with alcohol, evaporating the tincture to a small bulk, treating this with warm water, evaporating the aqueous extract at a low temperature, rendering it alkaline with ammonia, or sodium carbonate, and extracting with acetic ether. On evaporating the resulting solution the base is left. It is only slightly soluble in ordinary ether, in benzol or in chloroform, but dissolves in water, acetic ether, amylic alcohol, and ordinary alcohol. It forms salts with acids, and its chloride is precipitated by platinic chloride, forming a double salt. The following reactions have been noted with solutions of erythrophleine :—

Picric acid : yellow-green precipitate.
Iodine, in potassium iodide : reddish-yellow precipitate.
Iodide of mercury and potassium : white precipitate.
Iodide of bismuth and cadmium : flocculent white precipitate.
Potassium bichromate : yellowish precipitate.
Mercuric chloride : white precipitate.
Auric chloride : whitish ,,
Palladic chloride : white ,,

In contact with manganese peroxide and sulphuric acid, it develops a violet colour (less intense than that produced under similar circumstances by strychnine), which soon changes to a dirty-brown.

Erythrophleine possesses very marked toxic properties, and must be placed amongst those poisons which act upon the heart.

Two milligrams injected under the skin of a frog's foot caused the cessation of the heart's action in five to eight minutes. The ventricles cease in systole, the auricles generally in diastole. The cessation of the cardiac muscle is succeeded by a torpor of all the muscles, during which death occurs. The double salt with platinic chloride produces the same effect as the base itself.

Atropine does not rally the action of the heart paralysed by erythrophleine, but curare delays the effects.

*E. Couminga* is a variety resembling *E. guineense*. All parts of it are poisonous, and the poison consists of an alkaloïd, of which the physiological effects are similar to those of erythrophleine.

C. H. P.

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## On the Synthesis of Indigo-blue.

By H. WICHELHAUS (Deut. Chem. Ges. Ber., ix, 1106).

THE author has repeated Engler and Emmerling's experiments on the artificial formation of indigo-blue, but has failed to obtain a trace of that substance.

J. R.

**Indigotin in Animals, or the Purple of the Ancients.** By A. and G. DE NEGRI (Gazzetta chimica italiana, v, 437—438).

THE authors have ascertained that the purple of the *Murex trecuculus* consists of two colouring principles, one of which is indigotin. In order to extract the latter in the crystalline state, the humour of the mollusc is exposed to the air until it becomes violet; it is then dissolved in glacial acetic acid and the solution is diluted with water agitated with chloroform, which dissolves the purple. The residue left on evaporation, after being washed with ether to remove a red colouring matter, yields pure crystallised indigotin on allowing the alcoholic solution to evaporate. The purple from the *M. brandaris* is produced only on exposure to light, whilst that from *M. trecuculus* is formed equally well in the dark. *Elyria viridis* and some other molluscs contain chlorophyll.

C. E. G.

**On Apiin.** By E. VON GERICHTEN (Deut. Chem. Ges. Ber., ix, 1121—1126).

THE results of the author's examination of this substance agree in general with those previously arrived at by other chemists. Apiin rotates a ray of polarised light more powerfully than any other known substance: for yellow light $[\alpha]_y = +173°$. It contains 53·35 p. c. carbon, 5·36 p. c. hydrogen. When boiled with hydrochloric acid of sp. gr. 1·04 it deposits yellowish flocks of apigenin, which crystallise from alcohol in pearly laminæ. At the same time glucose, amounting to 41—45 p. c. of the apiin employed is set free. Apigenin contains 66·01 p. c. carbon, 3·83 p. c. hydrogen (mean of three analyses).

J. R.

**Note on Picrotoxin.** By R. APJOHN (Chem. News, xxxiii, 265).

REPEATED experiments prove that picrotoxin has a definite melting point (192°); that it does not undergo decomposition at this temperature; and that the crystals deposited from a water solution contain no water of crystallisation.

F. J. L.

**Products of Decomposition of the Biliary Acids.** By J. LANG (Deut. Chem. Ges. Ber., ix, 853).

SALTS of taurin have been prepared with silver, mercury (per-salts), lead, cadmium, calcium, and sodium. Of these the mercury salt, by its easy preparation and difficult solubility, is well adapted both for the preparation of pure taurin and its detection. By the same method by which benzoglycollic acid is formed from hippuric acid, a corresponding chologlycollic acid was obtained, and its barium, sodium, and silver salts were examined. An attempt to reproduce glycocollic acid from its two components, just as Dessaigne obtained hippuric acid by

heating benzoic acid with glycocine, resulted in the formation of an indifferent substance, *glycodystysin*, $C_{26}H_{39}NO_4$. The same body is obtained by heating glycocollic acid.

G. T. A.

# Physiological Chemistry.

## On Conjugated Sulphuric Acids in the Organism.

By E. BAUMANN (Pflüger's Archiv. f. Physiologie, xiii, 285—308).

THE author has previously applied the term "conjugated sulphuric acids" to acids which, on heating with the stronger mineral acids, become split into sulphuric acid and other different bodies (this Journal, 1876, i. 726). He found the salts of these acids in the urine of mammalia. The quantity present in the urine varies in different animals: a vegetable diet appears to increase them.

*The Phenol-forming Substance of the Urine.*—The author obtained the potash salt of this substance as follows:—If the alcoholic extract of horse's urine be evaporated to a syrupy consistence, and allowed to stand several days in the winter, crystalline scales then separate. These are drawn through a small linen filter, pressed between paper, and crystallised from water and afterwards repeatedly from strong spirit. They are soluble in about 10 parts of cold water, less so in spirit, almost insoluble in cold, but more soluble in boiling alcohol. Analyses showed the composition of this salt to be aproximately $C_6H_5KSO_4$. The author thinks that the substance first obtained from horse's urine is a mixture of a salt having the above formula, with another perhaps very similar to it, and containing more carbon, which can be only imperfectly separated by crystallisation.

*Behaviour of Phenol in the Animal Body.*— From the urine of patients treated with carbolic acid, the author obtained, by distillation after acidification, large quantities of phenol. The quantity of conjugated sulphuric acid is also much increased and amounts to 10 or 15 times the normal quantity. The author also obtained crystals of phenol-sulphate of potassium from the urine of patients who were treated externally with carbolic acid.

With regard to the *formation of conjugated sulphuric acids in the animal body* the author finds experimentally that, after the administration of large quantities of phenol, the sulphates present in the body (which had been introduced as sulphate of soda) appear in the urine as phenol-sulphates. Further experiments, the author thinks, show that phenol introduced into the body soon passes over into a combination which, even when small quantities of phenol are administered, is more or less converted into phenol-sulphuric acid; if greater quantities of phenol have entered the body, a larger portion of the first phenol-compound is excreted with the phenol-sulphuric acid in the urine.

The correctness of this conclusion is, he thinks, shown by the experiment of feeding another animal with the first formed phenol-

compound, which can be obtained from the liver, when phenol-sulphuric acid appears in the urine. As regards the nature of this first-formed compound, the author can only say that it contains phenol in a manner similar to phenol-sulphuric acid, and gives off the same on heating with strong acids.

The author finds that phenol-sulphate of potassium is a non-poisonous salt, and can be administered to rabbits with impunity. He hence suggests sulphate of soda as a chemical antidote in carbolic acid poisoning.

*On Indican.*—The author experimented first with extracts of the leaves of *Isatis tinctoria.* He obtained indigo-forming substance from all parts of the plant except the blossom and fruit, and believes that the occurrence of indican is connected in some way with the presence of chlorophyll, as plants which had grown up in darkness and were destitute of chlorophyll, did not contain any.

The author administered indol to a dog, both hypodermically and by the stomach, and found a great increase in the excretion of conjugated sulphuric acid. Indican was also present in very large quantity. He therefore concludes that the indican of the animal body is a conjugated sulphuric acid.

Further investigations showed that oil of turpentine likewise produces conjugated sulphuric acid in the organism.

E. C. B.

**Contribution to the Knowledge of Peptones.** By ALBRECHT KOSSEL (Pflüger's Archiv. f. Physiologie, xiii, 309—320).

THE author believes, in opposition to Maly, that peptone does not give a precipitate with acetic acid and ferrocyanide of potassium, and that any precipitate occurring on the addition of these reagents would be due to the presence of a small quantity of unchanged albumin.

He confirms the views of previous observers, that the albumin-molecule, during pepsin-digestion, becomes poorer in carbon and nitrogen, that it therefore probably undergoes a hydration on oxidation.

Further, his experiments confirm the statement of Lubavin that the peptones (or at least a part of them) possess properties which are common to the amidic acids. In these respects the process of pepsin-digestion does not differ from the splitting of the albumin-molecule on boiling with water, acids, or alkalis, or when acted on by the ferment of decomposition; it differs, however, in giving rise to products which are not (at least at the commencement of the process) converted by the further action of the ferment into carbonic acid and ammonia. The author could detect no ammonia in digestion of albumin lasting 24 hours.

E. C. B.

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**On the Excretion of Potash Salts.** By AUG. DEHN (Pflüger's Archiv. f. Physiologie, xiii, 353—368).

IN the following experiments the author, like previous observers, made use of the chloride of platinum test. Chlorine he estimated by nitrate of silver, with addition of some neutral chromate of potash,

and urea according to Liebig's method with nitrate of mercury. His chief results are as follows :—

I. *Normal Urine.*—Experimenting on himself, the author found (from an examination of the urine on seven days) that, on a mixed diet, the average excretion of potassium chloride *per diem* is 4·5 grams, and that of dipotassic oxide 2·9 grams. The variations observed he considers due to the different food ingested. He shows for instance that Liebig's extract of meat contains in 100 grms., 15·74 grms. of potassium chloride, 10 grms. of potash, and 8·3018 grms. of potassium. A cup of good coffee he reckons contains ·1 grm. of potassium chloride, and beer sometimes as much as ·4729 grm. of the same salt per litre. The author observes that increased ingestion of water, and consequent excessive secretion of urine, gives rise to an increased excretion of potassium. He finds further, that under ordinary conditions, the proportion of potassium chloride to sodium chloride excreted is on an average as 1 to 1·35, but that change of nourishment produces variations of this proportion in either direction. After alluding to the powerful affinity existing between chlorine and potassium, and mentioning that potassium does not occur in the urine in sufficient quantity to combine with all the chlorine, the author lays down the rule that: In normal urine, all the potassium occurs in the form of chloride. If an excess of potassium (*e.g.*, in the form of phosphate) be introduced into the system, the plasma of the blood has to give up so much chlorine that all the phosphate may become converted into chloride of potassium. The consequent defect of sodium chloride produces a desire for common salt, on the introduction of which the blood regains its normal composition.

II. *Excessive Introduction of Potassium Chloride.*—The author describes an experiment on himself in which he took 2 grams of potassium chloride dissolved in 1,000 c.c. of water. The result was that not only were the 2 grams of chloride excreted, but also a considerable quantity of the same salt was withdrawn from the body. The elimination of the salt commences from 3 to 4 hours after its introduction, and may extend over more than one day. The greater part of the water in the above experiment (955 c.c.) was thrown off in a short time, almost unused, as its content of the chloride was less than normal. The author also finds that the introduction of potassium chloride causes the withdrawal of common salt from the system.

From experiments in which potassium chloride was administered, without any increase of water, the author finds that if there is an excess of potassium chloride in the blood, it does not immediately attract water, but a considerable part is soon excreted (the urine becoming more highly loaded with this salt), whereas the rest remains stored up in the blood, to be excreted at the next convenient opportunity.

With regard to the influence of potassium chloride on the excretion of urea, the author found that the introduction of this salt into the system increased the metamorphosis of tissue, and he concludes that nourishment rich in potassium has the same effect.

The introduction of potassium always gave rise to violent headache, in the case of the author, and he considers that the headache which in

many persons is produced by taking very strong coffee, is due to the amount of potassium chloride contained therein.

E. C. B.

**Milk-globules, and a New Theory of Churning.** By F. SOXHLET (Landw. Versuchs. Stat., xix, 118—155).

IT is generally supposed that the fat-globules of milk are contained within a thin membrane, which it is necessary to destroy, before the fat itself can be separated and extracted from the liquid in which the globules are suspended. The destruction of this membrane can be accomplished, it is said, in two ways; either mechanically, by the operation of churning, or chemically, by the solvent action of some reagent, such as potash or acetic acid. Now if it be true, that, as in the latter case, the action of acetic acid upon milk is really due to a solution of this globule-membrane, then it is clear that more acetic acid must be used than would be required for the mere coagulation of the milk. Experiments, however, show that this is not the case. Again, if some milk be mixed with just enough very dilute acetic acid, to convert nearly the whole of its sodium phosphate into acid phosphate, but not sufficient to cause the separation of the casein, and a current of carbonic acid gas be passed through the liquid, perfect coagulation ensues, and the fat may then be extracted by shaking with ether.

These experiments seem, on the one hand, to indicate that the action of the acetic acid is to rob the milk of its emulsive condition, but, on the other hand, to refute the idea that it accomplishes this by the destruction of an enveloping membrane. In the precipitation of the casein by carbonic acid, the membrane-theory is inadmissible, because carbonic acid will not dissolve any single albuminous body.

The fact that the milk-globule, in its natural state, cannot be dissolved by ether, may be explained upon the assumption of a peculiar property of adhesion possessed by it, and this view is supported by the following experiment: if milk be dried in a vacuum over sulphuric acid, the fat can be easily extracted from the residue by ether; but if the residue be dissolved in water, the solution resists the action of the ether, just as milk does in its natural state.

Raspail (*Schmidt's Jahrb.*, vol. 24) cites in proof of the existence of a pellicle investing each globule, that the globules do not flow together. This may be answered by the parallel case of an emulsion of sugar-syrup and oil, in which the oil-drops no more tend to coalesce than the fat-globules in milk; and, similarly, by the case of the oil-drops in the *emulsio oleosa* of the German pharmacopœia, which differ from the fat-drops of milk only in being more transparent.

If quicksilver be shaken up with water, it separates into single globules, which cannot without trouble be re-united, the adhesion of the water to the surface of the globules preventing their flowing together.

It has frequently been asserted that a globule-membrane can be detected by the microscope, and Henle (*Froriep's Notizen*, 1839, 223) stated that a casein-membrane was visible after treatment with dilute

acetic acid. The author believes these opinions to be quite erroneous, and asserts that no membrane can be observed by the microscope, even with the aid of the highest powers.

There is another argument which has been advanced in proof of the existence of globule-membranes. Brücke (*Müller's Archiv.* 1847, 409) first called attention to the remarkable difference in specific gravity between butter-fat and the liquid in which it is suspended—a difference which, he observed, is sufficient to cause the fat to rise to the surface much more rapidly than it actually does. Brücke explained this difficulty by supposing each fat-globule to be enclosed within an envelope specifically heavier than the liquid, a deduction reasonable enough if milk-liquid could be compared to a solution of salt of the same specific gravity; but he had overlooked the fact that, like all albumin solutions, it is slightly gelatinous, a circumstance extremely likely to interfere with the rising of the globules to the surface.

The power of a gelatinous liquid to retain in suspension finely divided substances of a greater specific gravity than itself, was proved very clearly by Scheibler (Zeitschr. d. Vereins f. *Rübenzucker-Industrie in der österr.-ungar. Monarchie*, xi Jahrg., p. 435), who precipitated the baryta from a solution of barium arabate by sulphuric acid, and found that, after standing for four years, the fluid had remained just as milk-white as it was on the day on which the barium sulphate was thrown down.

From such considerations as these, the author believes the membrane theory to stand in direct opposition to our present chemical and physical knowledge, and he therefore abandons it. With regard to the condition in which the fat-globules exist, he believes that in new milk they are undoubtedly fluid drops, because, at the animal heat, the milk is at a higher temperature than the melting point of butter (34°—37°), and this view seems to be supported by their appearance when viewed under the microscope. But if milk be frozen at a temperature of three or four degrees below zero, the globules lose their fluidity, and become solid, and remain also in this state after the milk has been thawed. It was found that milk which had been thus treated could be churned into butter in 2 minutes, whereas to produce the same result with milk in its natural state required 11 minutes, showing that the low temperature had produced the same effect as 7—8 minutes churning.

The author concludes from this, that in the operation of churning, the liquid fat-globules are brought into the solid condition, but that this change can also be effected by subjecting the milk to a temperature of − 3° or − 4°.

H. H. B. S.

## On the Poisonous Action of Alcohols. By Dujardin, Beaumetz, and Audigé (Compt. rend., lxxxiii, 80—82).

This paper gives the results of experiments on the poisonous action of alcohols on dogs. The authors find that, of the alcohols produced by fermentation, the amount required to cause death within 24 hours varies with the atomic composition. The fatal dose per kilogram of

weight of the animal, administered by the stomach (I), and by hypodermic injection (II), was found to be—

| | I. | II. | |
|---|---|---|---|
| Of ethyl alcohol.... | 7·75 | 8·00 | grams. |
| ,, propyl ,, .... | 3·13 | 4·02 | ,, |
| ,, butyl ,, .... | 1·74 | 2·15 | ,, |
| ,, amyl ,, .... | 1·48 | 2·02 | ,, |

Experiments with other monatomic alcohols led to the following results:—

Methyl alcohol is more poisonous than ethyl alcohol, the fatal dose being 5 grams per kilogram of weight of the dog.

Heptyl and octyl alcohols vary in their action according as they are administered in the pure state or diluted with ethyl alcohol. The fatal dose of the pure substances is about the same as that of ethyl alcohol; but when diluted to ten times their bulk with absolute alcohol, the doses of 2·3—2·5 grams of heptyl alcohol, and 2—2·2 grams of octyl alcohol per kilogram of weight were found sufficient to cause death.

Cetyl alcohol, being insoluble, is not poisonous.

J. R.

## Chemistry of Vegetable Physiology and Agriculture.

### Formation of Ozone by the Contact of Plants with Peroxide of Hydrogen. By S. Cohné (Chem. News, xxxiv, 4).

The stem of a fresh plant inserted in a weak solution of hydric peroxide, rapidly decomposes it, with liberation of ozone and oxygen.

F. J. L.

### Weathering out of Aluminium Salts, and their Influence on Vegetation. By C. E. Bergstrand (Deut. Chem. Ges. Ber., ix, 857—858).

In the neighbourhood of Westerbotten, the sandy upper soil, poor in lime, often contains as much as 3 per. cent. of feather alum (hydrated aluminium sulphate). Although ·5 per cent. of this salt is usually fatal to vegetation, the *Rubus arcticus* was found to flourish in this neighbourhood. The ashes, amounting to 4·68 per cent. of the dry plant, may contain as much as 12·60 per cent. of sulphuric acid and 5·59 per cent. of alumina, but only about 5 per cent. of sulphuric acid, if grass and grain will grow on the soil.

G. T. A.

**Action of Sulphur in destroying Oïdium, and on the Emission of Hydrogen by Plants.** By E. POLLACCI (Gazzetta chimica italiana, v, 451—460).

BY a series of carefully conducted experiments, the author has ascertained that *Oïdium Tuckeri* is rapidly killed when exposed to an atmosphere containing sulphuretted hydrogen, and he also finds that grapes which have been sulphured give off sulphuretted hydrogen very slowly at 18° C., but rapidly and copiously at temperatures varying from 32°—38°. This was readily shown by washing the sulphured grapes with a small quantity of water, filtering the solution, and testing it with lead acetate and silver nitrate. Hence it follows that the chief action of sulphur in destroying Oïdium is due to the formation of sulphuretted hydrogen by the plant. This reaction takes place not only with grapes which have been attacked, but also with those which are in a healthy state. In fact, from experiments made with a large number of plants of different species, which in all cases gave sulphuretted hydrogen in contact with sulphur, the author concludes that all plants are capable of giving off nascent hydrogen.

C. E. G.

**On a Remarkable Case of the Reduction of Nitric Acid and Oxidation of Acetic Acid, with Production of Alcohol by the Influence of certain Microzymes.** By J. BÉCHAMP (Compt. rend., lxxxiii, 158).

THIS paper refutes M. Méhay's statement that in a mixture of solutions of acetate, nitrate, and phosphate of soda, the production of the glairy, nitrogenous, combustible substance, accompanied by reduction of the nitrate, with evolution of nitrogen, and conversion of the acetate into carbonate, is due to the presence of the phosphate, which sets up a sort of fermentation provoked solely by chemical reactions. The ferments, which are distinguishable by the microscope, consist of organised ferments, and are capable of determining the fermentation of sugar, &c. The phosphate of soda and other mineral matters furnish some of the elements requisite for the constitution of an organism.

C. H. P.

**Cellulosic Fermentation of Cane Sugar.** By E. DURIN (Compt. rend., lxxxiii, 128).

IN 1868 some beetroot juice was found to contain a quantity of white, rather hard clots, of unexplained origin. Subsequently a quantity of 50 hectolitres of a neutral solution of molasses, placed in a wooden vessel which had contained beet-juice, and the sides of which were covered with a slight deposit, was found twelve hours afterwards to be filled with clots in every way similar. There was evidently present some special ferment which transformed the sugar into an insoluble body, while the liquid in which this floated was rendered viscous.

The clots were found to be cellulose, and the viscosity of the liquid

was found to be due to a substance having a similar chemical composition, and differing only in physical properties.

The mother-liquor, which originally contained only cannose (saccharose), contained, after the cellulosic fermentation, a considerable amount of levulose. Cellulosic fermentation is not the same as viscous fermentation; all sugars can undergo the latter, but only cane-sugar can undergo the former. In viscous fermentation no clots are produced; in the cellulosic fermentation the viscosity is only accidental, and is frequently entirely absent.

In cellulosic fermentation proper no gas is evolved, but should the liquid become acid, carbonic anhydride escapes, some acetic acid is produced, and the inversion of the cannose proceeds independently of the cellulosic reaction. This reaction is thought to be the splitting up of a molecule of sugar, thus:—

$$C_{12}H_{22}O_{11} = C_6H_{10}O_5 + C_6H_{12}O_6.$$

Calcium carbonate favours the cellulosic fermentation by some special action, as well as by maintaining the alkalinity of the solution; but the carbonates of barium and magnesium, and calcium chloride hinder it. The development of the clots is more rapid in light than in darkness.

The ferment partakes of the nature of diastase. A solution containing 10 per cent. of pure sugar underwent cellulosic fermentation on the addition of some fresh diastase and a little precipitated calcium carbonate.

The fermentation proceeds best at a temperature of about 30°. Ebullition for four hours did not alter the properties of the diastase.

C. H. P.

## Note with reference to the Paper of M. Durin.

By L. Pasteur (Compt. rend., lxxxiii, 176).

It is stated that in 1861 the author announced the fact that there were two sorts of viscous fermentation produced by two distinct organised ferments. To one of them is probably due the cellulosic fermentation referred to in M. Durin's paper.

C. H. P.

## On the Fermentation of Fruits, and the Diffusion of the Germs of Alcoholic Ferments. By L. Pasteur (Compt. rend., lxxxiii, 173).

The germs which excite alcoholic fermentation are very abundant upon the bunches of ripe grapes, but very rare in the air. The germs lose their fecundity by drying at the ordinary temperature, in a few months, even upon the wood of the bunches.

For this reason, even perfectly ripe grapes, when crushed in small quantities in contact with the air, frequently do not ferment.

Experiments made with strawberries, cherries, and currants, show that, before maturity, those fruits do not exhibit any fruitful germs of alcoholic fermentation. They do not ferment if crushed in contact

with air; nor even cause the fermentation of sweet juices into which they are plunged whole. But, as with grapes, they ferment when a sufficient quantity of them is employed; and if the experiment be conducted on fruits more or less isolated, fermentation occurs or not, according to the presence or absence of fecund germs.

The ferments are more plentiful in summer than in winter, as may be shown by exposing freely to the air, for about 48 hours, a series of basins containing grape-juice, and then transferring their contents to bottles with long necks, projecting from boiling water. Fermentation will proceed in nearly every case, and a number of different germs may be recognised. In winter the experiment is but rarely successful.

C. H. P.

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## Intracellular Generation of the Alcoholic Ferment.

By L. FREMY (Compt. rend., lxxxiii, 180).

SOME cherries, carefully washed to remove possible germs from their surface, were placed in various bottles, some of which were filled with carbonic anhydride, others with hydrogen, and then hermetically sealed. In about a month they were opened, when it was found that carbonic anhydride had been evolved, and the fruits themselves contained alcohol.

Germs which excite alcoholic fermentation were found right in the interior of the fruits, from which Fremy infers the spontaneous generation of this organised ferment, but on this point Pasteur disagrees with him.

C. H. P.

## Influence of Physico-chemical Forces on the Phenomena of Fermentation.

By CH. BASTIAN (Compt. rend., lxxxiii, 159).

WHEN urine which has, by ebullition, been withdrawn from the influence of atmospheric germs, is neutralised with potash, treated with oxygen by means of an electric current passed through it, and heated to 50°, it becomes completely filled with bacteria in 7—12 hours. Every care having been taken in the experiments to prevent the introduction of possible atmospheric germs, it results that the fermentation of urine is totally independent of the germs which may exist in the air.

C. H. P.

## Note on the Alteration of Urine, with reference to Dr. Bastian's Paper.

By L. PASTEUR (Compt. rend., lxxxiii, 176).

THE statements contained in Dr. Bastian's paper are refuted, and the conclusions drawn from his experiments shown to be erroneous. A record of similar experiments by the author was published in 1862, wherein it is shown that the production or otherwise of bacteria in urine rendered alkaline with potash, is perfectly under the control of

the operator. If no extraneous germs are introduced, no bacteria are produced; whilst, if any germs are introduced, the mere fact of raising the temperature to 100° will not prevent their vivifying.

C. H. P.

**On the Fermentation of Urine.** By L. PASTEUR and J. JOUBERT (Compt. rend., lxxxiii, 5—8).

IN a recent paper by Musculus, that chemist stated, as the result of his experiments, that the ferment of urine has none of the properties of an organised ferment, but resembles rather the soluble ferments, such as diastase. Experiments made by the authors of the present paper lead them to agree with Musculus that there exists a soluble ferment capable of converting urea into ammonium carbonate. They find, however, that whenever urea or urine becomes alkaline, the change is accompanied by the development of microscopic organisms. Normal urine which does not contain the germs of this organised ferment, remains acid indefinitely in contact with air. The explanation of these apparently contradictory facts is as follows:—The soluble ferment of Musculus is produced by the organised ferment of urea, and it is freely formed, even in the absence of urea, in urinary and other liquids in which the organised ferment can live and grow.

This is the first known example of an organised ferment which forms, during its development, a soluble substance capable of producing the same fermentation as the organised ferment itself. Such is not the case with other ferments. Beer-yeast, for example, produces a soluble ferment which inverts cane-sugar, but does not act like yeast upon glucose. But the urea ferments, both organised and soluble, act in the same manner on urea: for the presence of the soluble ferment implies the previous existence of the organised, and, conversely, the organised ferment in its growth necessarily gives rise to the soluble ferment.

J. R.

**Antiseptic Properties of Borax.** By M. BEDOIN (Compt. rend., lxxxii, 1169).

FRESH meat corked up in a bottle filled with saturated solution of borax, was found fresh 5½ days after, and showed no trace of any living organisms, whereas meat similarly corked up with river water, was found to give off the peculiar ammoniacal odour of decomposing animal substances, and the liquid was full of bacteria in lively movement.

R. R.

# Analytical Chemistry.

## Testing for Nitric Acid in Natural Waters and other very Dilute Solutions thereof. By R. FRESENIUS (Zeitsch. Anal. Chem., 1876, 230—232).

KÄMMERER doubts two points in Fresenius' method for determining nitric acid in waters and very dilute solutions, depending on distilling the water acidified with acetic acid, and collecting the distillate in a solution containing potassium iodide and starch and acidified with sulphuric acid. He thinks that, in the first place, on warming the water, nitrous acid might be formed in consequence of the reduction of nitrates by organic matter, and that, therefore, according to this method, nitrous acid might be found where it did not pre-exist; and, secondly, that nitrous acid present in the water might be liberated by acetic acid, and then, during the warming of the water, further reduced by organic matter to nitric oxide, nitrogen, or ammonia and thus be lost, even where it was present in large quantities.

Plugge (*Zeitschr. Anal. Chem.*, xiv, 136) has proved that the first objection is unfounded, not only as regards natural waters, but even with respect to liquids containing large quantities of strongly reducing organic substances (grape-sugar, peptone, &c.); and Gratama (*ibid.*, xiv, 72), had previously shown that Kämmerer's assumed reduction of nitrates to nitrites by acidifying natural waters containing organic matter does not really take place. By a large number of experiments made by the author with grape-sugar and humic acid—in which no decomposition of the nitrous acid took place—Kämmerer's second supposition is shown to be unsupported by evidence.

It is, of course, necessary that this method should, like any other, be applied with due consideration of all conditions; for Meusel has shown, that nitrates dissolved in water are, in presence of carbo-hydrates, reduced to nitrites by bacteria, and it is obvious that substances could be added to solutions containing nitrous salts, which would decompose the acid liberated, or that such substances could exist even in natural waters under abnormal conditions.

D. B.

## Method for the Analysis of Alkaline Mineral Waters. By R. FRESENIUS (Zeitschr. Anal. Chem., xv, 221—230).

THE author had occasion to examine, in the course of last year, the five mineral wells of Neudorf in Bohemia, and other waters, all of which contained sodium bicarbonate, whereby his method mentioned in *Anleitung zur quant. Analyse*, 5th edit., § 209, &c., could be again tried, when he found that several points required alterations and improvements. The following is a complete method of analysing alkaline and ferruginous mineral waters.

*a. Determination of Chlorine, Bromine, and Iodine mixed.*—About 2000 grms. of water are evaporated on a water-bath to one quarter

of its original bulk. The solution is filtered, washed, the filtrate acidified with nitric acid, precipitated with argentic nitrate and the precipitate weighed either as such or after ignition in a stream of hydrogen.

*b. Determination of Silicic Acid, Iron, Manganese, Alumina, Lime, and Magnesia.*—About 7000 grms. of water are acidified and evaporated to dryness in large platinum dishes. The residue is moistened with hydrochloric acid, water added, the solution warmed, and the silicic acid filtered off and washed. After weighing, the silica is ignited with ammonium fluoride and sulphuric acid. Any non-volatile substances are deducted. The silicic acid filtrate is treated with ammonia, and the precipitate is filtered after warming and then washed. The latter (mostly hydrated ferric oxide) is dissolved in hydrochloric acid, neutralized with ammonium carbonate, boiled and filtered. Should ammonia give a precipitate in the filtrate, it is filtered separately, dissolved and reprecipitated. The filtrates are put together. The two precipitates are again dissolved, the solution treated with chemically pure alcohol (free from alumina), ammonia added, and the iron precipitated with ammonium sulphide. Having thus separated the iron from the alumina and the phosphoric acid, the ferrous sulphide precipitate is dissolved in hydrochloric acid, the solution oxidized with nitric acid, precipitated with ammonia, and weighed after ignition as ferric oxide. The filtrate from the sulphide is evaporated to dryness in a platinum dish, with addition of a solution of sodium carbonate, and the residue is heated with nitre. After moistening with water, it is dissolved in hydrochloric acid, and the solution is filtered and precipitated with ammonia. Traces of a flocculent precipitate of aluminium phosphate are generally obtained. The filtrates containing the manganese, lime, and magnesia are concentrated; the manganese is precipitated with ammonium sulphide; the precipitate, after 24 hours, collected on a filter, redissolved and reprecipitated; the precipitate mixed with sulphur and ignited in a stream of hydrogen; and the manganese weighed as sulphide. The filtrates are evaporated with hydrochloric acid, the sulphur filtered off, and the lime precipitated in the filtrate with ammonia and ammonium oxalate. The precipitate is redissolved and reprecipitated, and finally weighed either as carbonate or oxide. The filtrates are evaporated to dryness; the ammonia salts expelled by ignition; the residue is moistened with hydrochloric acid and evaporated to dryness, again taken up with hydrochloric acid and water; and the magnesia is precipitated with sodium phosphate and weighed as pyrophosphate.

*c. Determination of the Sulphuric Acid and the Alkalis*—About 3000 grms. of the water are acidified with hydrochloric acid, evaporated, and the silicic acid filtered off as in *b*. The filtrate, which must not contain much hydrochloric acid, is precipitated at the boiling heat by carefully adding barium chloride. The precipitate is first weighed, then warmed with hydrochloric acid and thoroughly washed The solution is evaporated to dryness with a few drops of barium chloride solution, dissolved in water, filtered, and the precipitate weighed with the former. The last weight is regarded as the most accurate. The filtrate is evaporated to dryness, the residue taken up with water,

and the solution boiled with addition of pure milk of lime. The filtrate is precipitated with ammonium carbonate and oxalate. The filtrate from the precipitate is evaporated to dryness, the ammonia expelled by ignition in a platinum dish, and the separation of the magnesia repeated, using very small quantities of the reagents. After expulsion of the ammonia-salts the alkaline chlorides are obtained. In order to separate the potassium chloride from the sodium and lithium chlorides, all three are converted in platino-chlorides, and the dry percipitate, after treatment with alcohol of 80 vol. p.c., is filtered and washed with alcohol. The potassium salt, having been transferred to a small tared platinum capsule, the remainder on the filter is dissolved in boiling water, evaporated to dryness, and weighed at 130°. To test the purity of the potassium-platino-chloride, it is again treated with water, platinum chloride and alcohol as above mentioned. The last weight is regarded as the most accurate. The quantity of sodium chloride is obtained by deducting the quantity of potassium chloride and lithium chloride (determined by the method described below) from the total sum of alkaline chlorides. Traces of alkaline earths, if present, must be determined and deducted from the total alkaline chlorides.

*d. Determination of the Carbonic Acid.*—The process as described in *Anleitung zur quant. Analyse*, 6 Aufl., p. 436, &c., is used.

*e. Determination of the Solid Residue.*—About 500—1000 grms. are evaporated in a tared platinum dish on a water-bath, and the residue is dried at 180° and weighed. It is treated with water and hydrochloric acid, then with excess of sulphuric acid, evaporated to dryness, and ignited for some time with addition of solid ammonium carbonate, so as to convert the acid sulphates of the alkalis in neutral sulphates (till constant in weight).

The solid residue of ferruginous waters is best determined with the water of bottles in which the iron has been completely deposited as hydrated ferric oxide by the action of the air. The solution is filtered and the filtrate treated as in the preceding case. The precipitate is dissolved in nitric acid; silicic acid if present is determined and added. The nitric acid solution is evaporated—the residue ignited, treated with water and ammonium carbonate, then heated moderately and weighed; and the weight is added to that obtained by weighing the solid residue of the filtrate at 180°. The ferric oxide, &c., is treated with nitric and sulphuric acids, evaporated and ignited. The weight obtained is added to the weight of sulphates.

*f. Determination of Iodine, Bromine, Lithium (Manganese), Barium, and Strontium.*—About 60 litres are evaporated in a tinned-copper still to about 4 or 5 litres, the alkaline liquid is filtered and the residue washed with hot water until the washings are free from alkali. The residue is also tested in the spectrum until a lithium line is no longer visible. The solution $\alpha$ serves for determining iodine, bromine, and lithium, and the residue $\beta$ for determining the (manganese) barium and strontium.

$\alpha$. *The solution* is evaporated and alcohol (95 p. c.) added, with constant mixing; the filtered residue is boiled three times with the alcohol; and the alcoholic solution is distilled over, with addition of two drops of strong potash-ley. The residue is dissolved in water,

evaporated, and again treated with alcohol of 96 p. c. The solution is redistilled and the residue again treated as above. An alcoholic solution is thus obtained which contains all the iodine and bromine, but only traces of alkaline chloride. The solution is evaporated in a platinum dish with addition of two drops of potash-ley, and the residue, after gentle ignition, is extracted with boiling water. If the solution be coloured brownish it is again evaporated with two drops of potash-ley and a small quantity of nitre, and the residue is again heated moderately. The solution, now colourless, is treated with carbon bisulphide and acidified with dilute sulphuric acid; a small quantity of a solution of nitrous acid in sulphuric acid is then added, with agitation; and the violet-coloured carbon disulphide is washed out. The iodine is determined in this liquid with a very dilute solution of sodium thiosulphate. From the solution left after washing out the iodiferous carbon disulphide, bromine and chlorine are precipitated in the form of silver-compounds, and the bromine is determined by deducting the weight obtained by heating weighed quantities of the bromo-chloride of silver in a stream of chlorine. The filtrate from the silver-compounds is treated with hydrochloric acid and filtered, and the filtrate is set aside.

For the determination of lithium (*a*) the three residues left by the treatment with alcohol (*b*), the two incinerated filters through which the solution (free from organic matter) of the alkaline metals was filtered, and (*c*) the solution which was obtained after separating the excess of silver, are used. The three are mixed together with water and then hydrochloric acid is added and the solution evaporated. The residue is treated with absolute alcohol and filtered, and the residue is boiled with small quantities of strong alcohol until either the residue of sodium chloride, or the evaporated residue of the last alcoholic extract, no longer gives a lithium-spectrum. The alcoholic filtrates are distilled off, the residue dissolved in water, with addition of two drops of hydrochloric acid, the solution is evaporated, and the treatment with absolute alcohol twice repeated, adding to the last alcohol used half its volume of ether, and always testing the residues by the spectrum. The ethereal-alcoholic solution is now distilled off; the residue moistened with water; hydrochloric acid added; the liquid again evaporated to dryness; the residue taken up with water; and to remove small portions of phosphoric acid which may have gone over into the solution, two drops of iron solution are added. Pure milk of lime is next added in slight excess, the mixture boiled, and the precipitate (mainly magnesium hydrate) filtered and washed with hot water until it no longer shows a lithium reaction. The filtrate is precipitated with ammonium oxalate, and the precipitate washed, ignited, dissolved, evaporated and tested for lithium. If a reaction be still obtained, the solution is again precipitated and filtered. The filtrate or filtrates are evaporated to dryness; the ammonia salts expelled; the residue moistened with hydrochloric acid; water added; the solution evaporated to dryness on a water-bath; and the treatment with milk of lime, &c., repeated, using small quantities of the reagents and constantly testing the separated precipitates for lithium. Having expelled the ammonia salts a second time, moistened with hydrochloric acid and evaporated,

the lithium is separated as lithium phosphate, according to the method mentioned in *Zeitschr. Anal. Chem.*, i, 42. The precipitate is then dissolved in hydrochloric acid, and tested to find out whether the dilute solution gives with excess of ammonia a small precipitate in the cold. If such be the case, it is redissolved in hydrochloric acid, precipitated with ammonia, filtered, weighed, and deducted from the lithium phosphate obtained. The filtrate from the phosphate is tested for caesium and rubidium.

β. *The residue insoluble in water* is treated with water in a large porcelain dish, and hydrochloric acid (with five drops of sulphuric acid) added. Solids adhering to the copper still are removed by treatment with acetic acid, and the whole is evaporated to dryness. The residue is treated with hydrochloric acid and water; the silicic acid, &c., filtered off; the precipitate boiled with sodium carbonate, until the silicic acid is dissolved; the solution filtered; and the residue washed, incinerated and fused with sodium carbonate. The fused mass is boiled with water, filtered, washed, and dissolved in dilute hydrochloric acid; the solution is evaporated; and the residue is taken up with water and a few drops of hydrochloric acid. The solution is then precipitated with a few drops of dilute sulphuric acid, left to settle, filtered, and the filtrate is treated with three vols. of alcohol. If a precipitate is formed, it is strontium sulphate or calcium sulphate. The filtered barium sulphate is, after washing, brought into a funnel closed at the bottom by a tap, and treated with a concentrated solution of ammonium carbonate. After 12 hours the tap is opened, the liquid run out very slowly, the precipitate washed and treated with very dilute nitric acid—to remove any strontium mixed therewith—then washed with water, dried, ignited and weighed as pure barium sulphate. The filtrate from the silicic acid is diluted with water, treated while warm with sulphuretted hydrogen—to remove traces of tin gone over into the solution—the filtrate is then boiled with nitric acid, the precipitate dissolved in hydrochloric acid, the ferric oxide separated by precipitation as basic salt, and the filtrate supersaturated with ammonia. In the solution, filtered, if necessary, the manganese is precipitated with ammonium sulphide, and the lime in the filtrate precipitated with ammonia and carbonate of ammonia. The filtered and washed precipitate is dissolved in nitric acid (adding the above-mentioned nitric acid solution containing strontium), and evaporated in a retort on a sand-bath, exhausting the moisture by means of an air pump. The residue is then treated with not too large a quantity of ether and alcohol, so as to dissolve the nitrate of calcium. The residue is dissolved in water, evaporated to a small bulk, and a concentrated solution of ammonium sulphate (1 in 4) added in excess. After 12 hours the solution is filtered through a small filter (the above-mentioned strontium precipitate obtained by the treatment with alcohol is added to the same), and after washing with ammonium sulphate, dried and ignited as sulphate.

*g. Determination of the Phosphoric Acid.*—The phosphoric acid might be estimated in the determination of the ferric oxide, alumina, &c., in *b* or in *f*. It is best, however, to determine it in a separate portion of the water. About 6 litres are evaporated with hydrochloric acid, the silicic acid is separated, the filtrate evaporated with nitric

acid to dryness, the residue dissolved in nitric acid and water, precipitated with a nitric acid solution of ammonium molybdate and the phosphoric acid determined as pyrophosphate of magnesia.

*h. Determination of the Nitric Acid and Ammonia.*—If nitric acid and ammonia are present in determinable quantities the method mentioned in *Anl. zur quant. anal.*, 5 *Aufl.*, pp. 696 and 697 is used. If the water contained large quantities of organic substances, it is better to replace the soda-ley necessary to expel the ammonia by magnesia.

D. B.

## Analysis of Sulphuretted Waters. By R. Fresenius (Zeitschr. Anal. Chem., xiv, 321—324).

I. *Estimation of Hydrogen Sulphide.*—Gravimetrically. A quantity of the water was collected directly in a bottle containing excess of cupric chloride and hydrochloric acid, and allowed to rest; the resulting precipitate filtered off, oxidised by a hydrochloric acid solution of bromine, and precipitated with barium chloride after removal of excess of acid.

Volumetrically. A sufficient quantity (found by previous experiment) of iodine-solution was placed in a 500 c.c. flask, and the water added until the colour disappeared. 5 c.c. of thin starch-paste were now introduced and subsequently sufficient iodine-solution to just produce a blue colour. Finally the liquid was made up to the mark with distilled water from a burette. The volume of the water taken is easily calculated, and from this the weight, on multiplying by the specific gravity. A correction must be made for the iodine required to produce a colour. The results of the two methods agree.

II. *Estimation of the Organic Matter.*—To prove the presence of volatile fatty acids, a large quantity of water was evaporated to a small bulk, filtered, neutralised with sulphuric acid, and then slightly acidified. It was now distilled, the distillate neutralised with baryta, evaporated to dryness, and the residue twice treated with warm absolute alcohol. The alcoholic solution obtained left, on evaporation, a residue which dissolved in water, and when subsequently dried and gently heated with sulphuric acid, gave off an acid vapour and smell of volatile fatty acids.

For the quantitative estimation of the remaining organic substances a quantity of water was evaporated and the well dried residue exhausted with alcohol. This gave a solution *a* and a residue *b*. The solution *a* left on evaporation a residue which dissolved in water, save a trace of resin. This was dissolved in alcohol, evaporated, dried, and weighed. The water solution was mixed with *b*.

*b* was treated with water, acidified with sulphuric acid and warmed to expel carbonic acid. Lead oxide was then added, the substance dried, mixed with excess of lead chromate and an organic analysis made. The resulting $CO_2$ (0·2324 grams) was calculated as humus substance ( = 0·1093).

F. J. L.

**The Analysis of Nitrates.** By F. JEAN (Bull. Soc. Chim. [2], xxv, 10—23).

THE author discusses the different methods which have been proposed for determining the quantity of nitric acid in commercial nitrates, manures, &c., the precautions which have to be taken, and the results which he has obtained.

C. S.

**A Test for Free Hydrochloric Acid in Presence of a Metallic Chloride.** By J. LÖWENTHAL (Zeitschr. Anal. Chem., xiv, 306—307).

THAT dioxide of lead is a sensitive test for free hydrochloric acid has been previously shown (*J. pr. Chem.*, lxxxv, 321 and 401). It is further found to be without action on chlorides of the formula MCl, but to liberate chlorine from ferric and stannic chlorides. Calcium chloride solution boiled with lead dioxide remains unchanged, but upon the addition of phosphoric acid, chlorine is evolved. This falsifies the statement of Richters and Junker (*Dingl. polyt. J.*, ccxi, 31), that phosphoric acid does not liberate chlorine from chlorides.

F. J. L.

**Estimation of Lithium by the Spectroscope.** By H. BALLMAN (Zeitschr. Anal. Chem., xiv, 297—301).

UPON diluting a solution of lithium chloride, a point is finally reached at which the spectroscopic line $Li_a$ disappears. Theoretically this limit is constant; practically it varies slightly. Experiments showed that if a solution of lithium chloride be diluted until the line $Li_a$ disappears, there is then contained in every 3345 c.c. of this solution 1·0 mg. of the salt. The flame and spectroscope should be fixed, and the solution introduced into the flame upon a cylindrical (not conical) spiral of platinum, after being dried by approximation to the burner. In estimating the lithium in solutions of unknown strength only a portion of the solution need be diluted to the extinction point. The lithium must exist as chloride. The presence of calcium chloride interferes with the reading of the extinction-point. Other metals possessing characteristic spectra may also be estimated in this manner.

F. J. L.

**New Method of Separating Nickel and Cobalt.** By A. GUYARD (Bull. Soc. Chim. [2], xxv, 509).

THE nickel and cobalt are separated in the usual way from the metals associated with them, and then both are precipitated with a very slight excess of ammonium sulphide; the bulk of the liquid containing the suspended sulphides is increased by the addition of water, and then a dilute solution of potassium cyanide added carefully, so as to avoid excess. The nickel sulphide being completely and readily soluble in cold very dilute solution of potassium cyanide, and the cobalt sulphide

being perfectly insoluble in that medium, it is easy to see the progress of the reaction by the clearing of the liquid, in which the cobalt sulphide floats in detached particles. The liquid is then filtered, the cobalt sulphide being collected and estimated in the usual way.

The filtrate containing the nickel is then slightly acidulated with hydrochloric or sulphuric acids, whereby the nickel cyanide is thrown down; this is then collected on a filter, washed and ignited, and the nickel oxide is weighed.

The nickel oxide is frequently contaminated with silica, which, in accurate work, must of course be removed before weighing.

C. H. P.

**Action of Zinc on Solutions of Cobalt.** By LECOQ DE BOISBAUDRAN (Bull Soc. Chim. [2], xxv, 538).

IT is found that although cobalt is not precipitated from its solutions by metallic zinc, the presence of a metal easily reduced by zinc determines the precipitation of the cobalt. Lead and copper both act in this way, the latter in particular; cadmium does not. The solution should be very nearly neutral for copper to produce the maximum effect; if the liquid is very acid, the copper alone is deposited. In a solution rendered very basic by lengthened contact with zinc, the cobalt is not only no longer precipitated, but actually redissolves, at the same time an insoluble subsalt of copper is produced. The addition of a very minute quantity of acid again decolorises the solution. The cobalt is reduced to the metallic state; the metallic sponge is at first attacked by hydrochloric acid, but the action soon ceases, which indicates an intimate admixture of the copper and cobalt. One specimen retained four-fifths of its cobalt after immersion for 48 hours in strong hydrochloric acid.

The presence of a definite quantity of copper-salt is necessary, for if the amount present is too small, only part of the cobalt is reduced; a further addition of copper-salt determines a further separation of cobalt.

C. H. P.

**Estimation of Carbon Bisulphide, Copper, and Caustic Alkalis by means of Potassium Xanthate.** By E. A. GRETE (Deut. Chem. Ges. Ber., ix, 921—924).

THE author bases his volumetric method of analysis on the reaction between cupric salts and xanthates, previously employed by Vogel for the detection of carbon bisulphide in coal gas.

*Carbon bisulphide* is estimated by first converting it into potassium xanthate by the known method, and adding thereto a solution of copper of known strength until a precipitate is no longer produced. The copper xanthate thrown down settles well after agitation, so that the end of the reaction is easily recognised. Excess of caustic potash remaining after the formation of xanthate must be neutralised with acid potassium tartrate, or, better, sodium bicarbonate, before adding the copper solution.

The copper solution is made by dissolving 3·168 grams of copper, in the form of pure sulphate, in water, adding sodium and potassium tartrate and sodium carbonate in sufficient quantity to redissolve the precipitate first thrown drown, and making up the volume to 1 litre. Caustic alkalis and ammonia must be avoided, as they interfere with the correctness of the results. 1 c.c. of this solution corresponds with 0·0076 gram of carbon bisulphide.

*Copper* is estimated by the converse process, namely, by dissolving it, in the form of soluble salt, in water, adding to the solution sodium carbonate and sodium and potassium tartrate, and precipitating with a solution of a xanthate of known strength. The results are accurate.

*Caustic alkalis* are estimated by dissolving them in as dry a state as possible in absolute alcohol, converting them into xanthates by the addition of carbon bisulphide, and titrating with copper solution.

J. R.

## Influence of certain Salts and of Lime in Saccharimetry.

By A. MÜNTZ (Compt. rend., lxxxii, 1334—1336).

THE rotatory power of a solution of cane-sugar is affected by certain substances which have themselves no action on polarised light or on sugar. Salts of the alkalis and alkaline earths reduce the rotatory power in very varying degrees, whilst salts of the heavy metals, such as zinc and lead, have little or no effect.

A large number of salts, including the sulphates, nitrates, and acetates of sodium, potassium, ammonium, and magnesium, the phosphates of sodium, potassium, and ammonium, chlorate, sulphite, and hyposulphite of sodium, the chlorides of calcium, magnesium, barium, &c., must be present in large proportion to produce a marked effect, as much as 20—30 parts to 100 parts of sugar being required to reduce the deviation 3 or 4 degrees. Other salts, as sodium borate, carbonate, and chloride, potassium carbonate, &c., have a greater influence.

Neutral lead acetate, even in the proportion of 25 grams to 100 c.c. of sugar-solution, does not affect the rotatory power. Lime, however, reduces it considerably.

The author concludes, from the results of his observations,—(1) that though the presence of salts in raw sugars tends to falsify the results of polarimetric analysis, the errors thus introduced are in most cases so small that they may be neglected; (2) that sodium carbonate or sulphate should not be employed to precipitate excess of lead from sugar-solutions, as is done by some chemists; (3) that lead acetate, even in excess, is without influence on the rotatory power of sugar.

J. R.

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## Detection of Sulphur in Organic Compounds. By H. VOHL (Deut. Chem. Ges. Ber., ix, 875—877).

IN a paper on methenyldiphenyldiamine contributed to the Berlin Chemical Society (*Berichte*, ix, 456), Weith stated that, for the detec-

tion of sulphur, he had used a method published by Bunsen (*Ann. Chim. Pharm.*, cxxxviii, 226), and afterwards by Schönn (*Zeitschr. f. Chem.*, 1869, 664), which consisted in heating the substance with sodium, and testing for the sodium sulphide with sodium nitroprusside.

Vohl observes that as this method had been used and published by him as early as 1863 (*Ding. polyt. J.*, clxviii, 49; *Zeitschr. f. Anal. Chem.*, ii, 442; *Jahresb. f. Chem.*, 1863, 777), it could not have originated with either Bunsen or Schönn, the former having mentioned it for the first time in 1866, and the latter in 1869.

H. H. B. S.

**Estimation of Anthracene in Coal Tar.** By CARL NICOL (Zeitchr. Anal. Chem., xiv, 318—321).

THE method, like that of Luck (*Zeitschr. Anal. Chem.*, xii, 347, and xiii, 251), depends upon the insolubility of anthraquinone in cold dilute acetic acid.

About 10 to 20 grams of the tar are placed in a retort, which is connected with a U-tube contained in a paraffin bath at 200°. The retort is gradually heated, the temperature being slowly raised until all volatile matters have passed over. Care must be taken to prevent bumping, and also the condensation of the distillate upon the top and neck of the retort. Finally, there remains in the retort a porous mass, and in the U-tube all the volatile constituents whose boiling point is above 200°. The portion of the neck containing condensed substance is cut off, ground up, and the pieces inserted in the U-tube. The distillate is now completely dissolved by repeated warming with acetic acid. Oxidation is proceeded with by means of chromic acid according to the directions of Luck, and the anthraquinone thus formed is precipitated by water and collected on a filter.

F. J. L.

**Estimation of Phosphoric Acid in Guano.** By C. SCHUMANN (*ibid.*, 301—303).—The guano is boiled in dilute nitric acid (1 in 10) for half-an-hour, the liquid diluted, and filtered, and the phosphoric acid determined in a portion of the filtrate by the molybdenum method. This process saves heating the guano to redness, or fusing with chlorates to destroy organic matter, and gives accurate results.

**Rotatory Power of Grape Sugar.** By F. HOPPE-SEYLER (*ibid.*, 303—306).—The rotation of sugar varying, according to different experimenters, from 50° to 57°, experiments were made with great care on sugar obtained from diabetic urine and purified by repeated crystallisation from alcohol. The average of the rotations obtained was (for sodium colour) 564; the rotary constant 1773. The rotary constant does not vary with the concentration of the liquid.

**An Arrangement for essentially accelerating Filtration with the Air-pump.** By W. HEMPEL (*ibid.*, 308).—This consists in

etching upon the funnel fine lines running from about 9—12 mm. beneath the edge of the filter paper down to the stem.

**Precipitation of Zinc by Hydrogen Sulphide in Presence of Hydro-potassic Sulphate.** By G. SEELHORST (*Zeitschr. Anal. Chem.*, 316).—From a solution which contains hydro-potassic sulphate, and has a strong acid reaction, zinc is precipitated by hydrogen sulphide.

**Concentrated Sulphuric Acid as a Test for Molybdic Acid.** By F. VON KOBELL (*ibid.*, 317.)—This test, attributed to Schönn and Maschke, the author made known in 1831; more fully in 1838 in his "Outlines of Mineralogy."

**Note on Water Analysis.** By S. W. RICH (*Chem. News*, xxxiii, 235).—In the estimation of free and albuminoïd ammonia in waters containing but small quantities thereof, the various distillates are collected and redistilled, whereby the whole of the ammonia is obtained in a small quantity of liquid, and therefore more accurately determined.

**Estimation of Tannin by Muntz and Ramspacher's Method.** By H. R. PROCTER (*ibid.*, 245).—It is found that the raw hide used in this method absorbs large quantities both of gallic acid and of hydrochloric acid.

**On the Action of certain kinds of Filters on Organic Substances.** By J. A. WANKLYN (*ibid.*, pp. 4, 11, 24).—Solutions of sulphate of quinine, and of hydrochloride of morphine and strychnine were found to be completely absorbed by a silicated carbon filter after repeated filtration.

**Estimation of Phosphoric Acid in Fertilisers.** By A. H. CHESTER (*ibid.*, 255).—The author's analyses by the magnesia method agree with those by the molybdenum process.

**Notes on Blowpipe Analysis.** By H. B. CORNWALL (*ibid.*, xxxiv, 27).—Von Kobell's potassic iodide and sulphur mixture, used as a test for bismuth, constitutes a delicate test for lead, even in presence of the former. Mercury-compounds, the sulphides of arsenic and antimony, and cadmium compounds, which give a similar yellow sublimate, may be removed by preliminary treatment with a moderate oxidising flame.

F. J. L.

## Technical Chemistry.

**Practical and Theoretical Study of Green, Blue, and Violet Ultramarine.** By E. DOLLFUS and F. GOPPELSRÖDER (Dingl. Polyt. J., ccxx, 337—348, and 431—444).

IN the first part of their paper the authors give a brief history of ultramarine. Since Tassaert and Kuhlmann, in 1814, observed the formation of a blue substance, the former in soda-kilns and the

latter in calcination-kilns, synthetical and analytical investigations relating to it have been carried on. Improvements have been made in the various analytical methods, and since Vauquelin regarded the artificial products as being identical with the natural ultramarine (lazulite), the authors think it advisable to subject the latter to a new analytical investigation, which they intend to do, as soon as a sufficient quantity of this rare mineral can be obtained.

About fifty years ago Guimet began to prepare ultramarine on a large scale; Gmelin followed him, and published his results, but although, since 1827, the manufacture of this article has been greatly modified, our knowledge of the chemical constitution of the different ultramarines, in spite of the valuable discoveries of Unger and R. Hoffmann, is still very limited.

It is well known that the most essential elements composing the ultramarines are aluminium, sodium, sulphur, and oxygen. Iron, calcium, potassium, and magnesium are occasionally present. On examining the three ultramarines in the spectrum, the sodium line alone is visible; the lines of potassium and the other metals are not seen, even when the ultramarine is decomposed with dilute hydrochloric acid, filtered, and the filtrate evaporated. To show the potassium line a careful separation of the different metals would have to be made, in order to obtain a mixture of the alkaline chlorides in a pure and concentrated state. Nitrogen could not be found in either of the three different qualities.

Brunner's views with regard to the chemical constitution of blue ultramarine are, that this substance is a compound of aluminium silicate with sodium sulphate and sulphide. Breunlin considers it a double silicate of aluminium and sodium in combination with five equivalents of sodium sulphide. To solve the question whether ultramarine could be obtained without the presence of silicic acid, Büchner calcined a mixture of sodium, aluminium, sulphur, and coal, and a second mixture containing, in addition to the above substances, silicic acid. After the calcination the mixture of $Al_2O_6Na_6 + 6S + 3C$ had a light blue colour; the soda-alum contained silicic acid. The mixture of $Al_2O_6Na_6 + 6S + 3C + 2SiO_2$ had assumed a dark blue colour.

Ritter has found that the gases evolved from blue ultramarine by acids contain sulphurous acid. He separates the sulphuretted hydrogen from the acid, by retaining it in a hydrochloric acid solution of tartar emetic, or arsenious acid. W. Stein concludes from his investigations that ultramarine contains sulphurous acid, but not thiosulphuric acid, and that neither sulphites nor thiosulphates are necessary in its composition. He thinks that the colour is due to black aluminium sulphide, which is formed at high temperatures by the action of sodium sulphide on aluminium, and therefore considers ultramarine not as a chemical compound, but as a mere mixture, the blue colour being caused by the optical properties of the substances composing the mixture. Aluminium sulphide is but very little known, and if it were contained in ultramarine, the latter would behave differently to chlorine. According to Gentell, aluminium chloride is not formed by the action of a stream of chlorine at a high temperature on ultramarine; under the same conditions the authors could convert only a small portion of the aluminium

into the chloride. Can we conclude from this that the aluminium is present as a silicate, or as a double compound of aluminium silicate with sodium silicate, in both cases combined with sulphur compounds? Or is the oxygen partly replaced by the sulphur? Contrary to Guignet's statements the authors could not find free sulphur by digesting ultramarine with carbon disulphide.

R. Hoffmann mentions that, on heating the aluminium silicate contained in the raw materials to a point at which the mass begins to soften, it combines with exactly a sufficient quantity of the sulphur compounds, melted in atomic proportions, to form the chemical molecule of ultramarine. The excess of sodium persulphide is absorbed by the ultramarine, and retained mechanically. If at this stage of the operation the influence of air is prevented, we obtain after cooling, in that part of the mass which is poor in silicic acid, white ultramarine, while in the part rich in silicic acid a product of a greenish-blue colour is obtained. As in the usual method the mass is cooled slowly, an oxidation results, the mass poor in silica being green, that rich in silica assuming a blue colour, and the excess of persulphide being converted into sulphate. Hoffmann distinguishes a siliciferous ultramarine decomposible by alum, called pure blue, and a reddish-blue ultramarine rich in silicic acid and not decomposible by alum. The proportion of aluminium oxide and silicic acid is, in the case of the former 1 : 1·28, of the latter 1 : 1·7. In a sample of green ultramarine the authors found the proportions 1 : 1·16, of blue ultramarine, 1 : 1·57, violet 1 : 1·83; the quantities of sulphur in the three colours were, after deducting iron, magnesium, calcium, gypsum, water, and kaolin, in the green 7·7 per cent., in the blue (DM) 13·4 per cent., and in the violet (VR 24) 12·4 per cent.

*Quantitative Analysis of the Ultramarines.*—For the determination of the sulphur, Hoffmann used potassium chlorate mixed with potassium and sodium carbonates, at the same time allowing caustic potash to act on the mixture. For determining the aluminium and silicic acid, the authors used bromine and dilute hydrochloric acid. Alumina, &c., was determined as usual; the alkalis were determined in the solution previously used for estimating the sulphur of the sulphuric acid. The excess of baryta, after filtering off the sulphate, was precipitated with ammonium carbonate, and the filtered solution evaporated and ignited. The residue was treated with water, the magnesium filtered off, the filtrate evaporated with sulphuric acid, and the residue again ignited with ammonium carbonate to convert the potassium bisulphate into sulphate. The lime sulphate was extracted with sodium thiosulphate and precipitated with ammonium oxalate. The lime oxalate was titrated and checked by a determination of the lime as carbonate. In the determination of the sulphur $a + b$ (after oxidation with bromine, &c.), and from SO, the sulphur was precipitated by ammonium carbonate and barium chloride added only to the filtrate. The sulphur from $S_2O_2$ could not be determined in this manner, as the solution did not allow heat to be applied, and as, in the cold, an incomplete precipitation takes place.

The composition of the clay residue was the following: 100 parts contain—

| | Green. | Blue DM. | Violet VR24. |
|---|---|---|---|
| Silicic acid..... | 52·471 | 52·846 | 49·582 |
| Aluminium oxide .. | 13·118 | 41·230 | 41·179 |
| Iron oxide ..... | 34·410 | 5·922 | 9·239 |
| | 99·999 | 99·998 | 100·000 |

The clay residue was determined by decomposing the ultramarines with hydrochloric acid, evaporating the filtrate, again treating residue with hydrochloric acid (dilute), filtering, and washing. The residue on the filter was dried, and boiled with soda together with the filter:

| | Green. | Blue. | Violet. |
|---|---|---|---|
| Kaolin..... | 0·526 per cent. | 3·039 per. cent. | 4·673 per cent. |
| Silicic acid .. | 0·276 „ | 1·606 „ | 2·254 „ |

In the residue from the violet, 0·127 p.c. of CaO was found.

The water was determined at 120°, and also, according to Hoffmann's method, passing the gases through a layer of granulated copper and absorbing them by calcium chloride.

Obtained—

I. Drying at 120°:—

| Green. | Blue. | Violet. |
|---|---|---|
| (1.) 0·686 per cent. | 2·024 per cent. | (1.) 5·419 per cent. |
| (2.) 0·940 „ | — | (2.) 6 337 „ |

Hoffmann's method:

| | | |
|---|---|---|
| 4·884 per cent. | 4·904 per cent. | (1.) 11·614 per cent. |
| | | (2.) 11·460 „ |

*Results of the Analyses of the Three Different Colours of Ultramarine used at the Works of Dollfus-Mieg, and Co.*

| | Green. | Blue (DM). | Violet (VR24). |
|---|---|---|---|
| Silicic acid ..... | 36·770 | 37·868 | 22·305 |
| Aluminium oxide .. | 31·499 | 24·285 | 12·790 |
| Iron oxide ..... | 0·181 | 0·180 | 0·420 |
| Sodium oxide..... | 13 401 | 12·009 | 6·855 |
| Potassium oxide.... | 0·408 | — | — |
| Magnesium oxide .. | traces | 0·063 | 0·506 |
| Calcium oxide .... | traces | 0·225 | — |
| Sulphuric acid .... | 0·693 | 1·104 | 1·004 |
| Sulphurous acid.... | 0·405 | 0·780 | 0·764 |
| Thiosulphuric acid.. | — | 0·621 | 1·742 |
| Sodium sulphide .. | 8·592 | 6·582 | 1·255 |
| Free sulphur ..... | 3·310 | 7·929 | 3·188 |
| Lime sulphate..... | traces | traces | 41·814 |
| Water according to R.H. ..... | 4·884 | 4·904 | 11·537 |
| | 100·215 | 96·550 | 104·180 |

*Results of the Analyses of Three Different Ultramarines, taking into account the quantity of Kaolin.*

| | Green. | Blue (D.M.) | Violet (VR24). |
|---|---|---|---|
| Silicic acid..... | 36·494 | 36·262 | 20·051 |
| Aluminium oxide .. | 31·430 | 23·032 | 10·918 |
| Iron „ .. | — | (kaolin, see below) | |
| Sodium „ .. | 13·401 | 12·009 | 6·855 |
| Potassium „ .. | 0·480 | — | — |
| Magnesium „ .. | traces | 0·063 | 0·506 |
| Calcium „ .. | traces | 0·225 | — |
| Sulphuric acid .. | 0·693 | 1·104 | 1·004 |
| Sulphurous „ .. | 0·405 | 0·780 | 0·764 |
| Thiosulphuric acid.. | — | 0·621 | 1·742 |
| Sodium sulphide .. | 8·592 | 6·582 | 1·255 |
| Free sulphur .. | 3·310 | 7·929 | 3·188 |
| Lime sulphate .. | traces | traces | 41·814 |
| Water .. | 4·884 | 4·904 | 11·537 |
| Kaolin .. | 0·526 | 3·039 | 4·546 |
| | 100·215 | 96·550 | 104·180 |

The residue of the kaolin contained:—

| | | | |
|---|---|---|---|
| Silicic acid..... | 52·471 | 58·846 | 49·582 |
| Aluminium oxide .. | 13·118 | 41·230 | 41·179 |
| Iron..... | 34·410 | 5·922 | 9·239 |

Iron oxide replaces the aluminium oxide according to the atomic proportions.

100 parts of the ultramarines free from iron, magnesium, calcium, lime sulphate, water and kaolin contain—

| | Green. | Blue. | Violet. |
|---|---|---|---|
| Silicic acid ..... | 38·494 (1·00) | 41·058 (1·06) | 43·801 (1·13) |
| Aluminium oxide .... | 33·152 (1·39) | 26·078 (1·09) | 23·850 (1·00) |
| Sodium „ .... | 14·135 (1·04) | 13·597 (1·00) | 14·975 (1·10) |
| Potassium „ .... | 0·506 (—) | — (—) | — (—) |
| Sulphuric acid..... | 0·731 (1·00) | 1·250 (1·71) | 2·193 (3·00) |
| Sulphurous „ ..... | 0·427 (1·00) | 0·883 (2·06) | 1·669 (3·90) |
| Thiosulphuric acid.... | — (—) | 0·703 (1·00) | 3·805 (5·40) |
| Sodium sulphide ..... | 9·063 (3·10) | 7·452 (2·62) | 2·841 (1·00) |
| Free sulphur ..... | 3·491 (1·00) | 8 977 (2·50) | 6·964 (1·99) |
| | 99·999 (—) | 99·998 (—) | 100·098 (—) |

100 parts contain therefore:—

| | Green. | | Blue (DM). | | Violet ($VB_{24}$). | |
|---|---|---|---|---|---|---|
| Silicon | 17·963 | | 19·160 | | 20·440 | |
| Aluminium | 17·702 | | 13·925 | | 12·735 | |
| Sodium from $Na_2O$ | 10·487 | Total sodium including Na from $Na_2S$ = 15·832. | 10·088 | Total Na = 14·483 | 11·110 | Total Na = 12·786 |
| Potassium | 0·420 | | — | | — | |
| Sulphur *c.* from $SO_3$ | 0·292 | Total sulphur = 7·714 | 0·500 | Total S = 13·414 | 0·877 | Total S = 12·376 |
| Sulphur *e.* from $SO_2$ | 0·213 | | 0·441 | | 0·834 | |
| Sulphur *d.* from $S_2O_2$ | — | | 0·469 | | 2·536 | |
| Sulphur *a.* from $Na_2S$ | 3·718 | | 3·057 | | 1·165 | |
| Free sulphur *b.* | 3·491 | | 8·977 | | 6·964 | |
| Sodium from $Na_2S$ | 5·345 | | 4·395 | | 1·676 | |
| Oxygen | 40·363 | | 38·984 | | 41·748 | |
| | 99·994 | | 99·996 | | 100·085 | |

| | | | |
|---|---|---|---|
| Oxygen in aluminium oxide | 15·450 | 12·153 | 11·115 |
| " " sodium " | 3·648 | 3·509 | 3·865 |
| " " potassium " | 0·086 | — | — |
| " disposable for the sulphur compounds | 21·179 | 23·322 | 26·768 |
| Total quantity of oxygen | 40·363 | 38·984 | 41·748 |
| " " sulphur *a*, *b*, *c*, *d*, *e* | 7·714 | 13·444 | 12·376 |
| Proportion of the quantity of sulphur to the quantity of oxygen disposable for the compounds with the sulphur | 1 : 2·740 | 1 : 1·730 | 1 : 2·160 |
| Proportion of the quantity of sulphur to the total quantity of oxygen | 1 : 5·200 | 1 : 2·900 | 1 : 3·300 |

The following table shows the action of different reagents on the three ultramarines, with special reference to the rapidity of the decomposition. 0 indicates no reaction. 1. Slow action. 2. Somewhat quicker. 3. Quick. 4. Very quick.

| Reagents. | Green. | | Blue (DM). | | Violet ($VR_{24}$). | |
|---|---|---|---|---|---|---|
| Dilute mineral acids | Decomposition | 4 | Decomposition | 4 | Decomposition | 2 |
| Citric acid in aqueous solution | " | 2 | " | 3 | " | 3 |
| Oxalic acid in aqueous solution | Decomposition ($H_2S$) | 1 | Decomposition ($H_2S$) | 1 | Decomposition ($SO_2$) | 4 |
| Concentrated acetic acid | " " | 1 | " " | 0 | " " | 1 |
| Dilute and cold alum solution | Decomposition | 1 | " " | 0 | " " | 0 |
| Concentrated and slightly warm alum solution | " | 4 | Decomposition | 2 | Decomposition | 1 |
| Boiling alum solution | " | 4 | " | 3 | " | 1 |
| Caustic solutions, concentrated and dilute, hot and cold | .. .. .. | 0 | .. .. .. | 0 | Turns blue | ½ |
| Alkaline solution of lead acetate | .. .. .. | 0 | .. .. .. | 0 | .. .. .. | 0 |
| A series of reducing substances (wet way) | .. .. .. | 0 | .. .. .. | 0 | .. .. .. | 0 |
| Ozone | .. .. .. | 0 | .. .. .. | 0 | .. .. .. | ½ |
| A series of oxidizing substances (wet way) | .. .. .. | 0 | .. .. .. | 0 | .. .. .. | 0 |
| Nitric acid silver solution with or without ammonia | .. .. .. | 0 | Bluish-green | 2 | .. .. .. | 0 |
| Bromine with water and addition of hydrochloric acid | Decomposition. Clay residue | 2 | Decomposition. Clay residue | 3 | Decomposition. Clay residue | 3 |
| Concentrated nitric acid | Decomposition | 4 | Decomposition | 4 | Decomposition | 4 |
| Heated to low redness | Bluish-green colour | 3 | .. .. .. | 0 | Blue colour | 4 |
| A higher temperature | Decoloration | 3 | Decoloration | 3 | Decoloration | 3 |
| Action of carbonic oxide at high temperatures | .. .. .. | 0 | .. .. .. | 0 | Blue colour | .. |
| Action of hydrogen at high temperatures | Brownish-yellow colour | .. | .. .. .. | 0 | " | .. |
| Action of arsenious acid at high temperatures | .. .. .. | 0 | Green colour | .. | Green, partly blue | .. |
| Action of arsenious acid at a still higher temperature | .. .. .. | 0 | .. .. .. | .. | Light blue | .. |
| Various oxidizing substances acting at moderate temperatures (dry way) | Blue colour | .. | .. .. .. | .. | Blue colour | .. |
| Various oxidizing substances acting at high temperatures (dry way) | Discoloration | .. | Decoloration | .. | Decoloration | .. |
| Action of chlorine (dry) at an increased temperature | Blue colour | .. | Bluish-violet | .. | Pink colour | .. |
| Action of chlorine (dry) at a high temperature | Discoloration | .. | Decoloration | .. | Decoloration | .. |
| Action of alkaline bodies at high temperatures | Decomposition | .. | Decomposition | .. | Decomposition | .. |
| Action of borax at high temperatures | .. .. .. | 0 | .. .. .. | 0 | Light-blue colour | .. |

Very dilute hydrochloric acid evolves traces of sulphuretted hydrogen and decolorises the three ultramarines after the lapse of five minutes. Potassium ferrocyanide does not act on the colourless solutions; the ferricyanide indicates only a slight green reaction. This fact shows that the iron of the ultramarines does not exist as a substitution-element of aluminium, because it remains undissolved even after treatment with concentrated acid, whereas the aluminium dissolves. The decomposition-product of the violet colour formed a powder, and that of the green and blue colours a gelatinous mass. Citric acid forms with the blue colour a body of a dirty white colour, with the violet a dirty yellowish-white substance, the filtrate of both being colourless. Oxalic acid readily decomposes the violet but acts only slowly on the green and blue colours, evolving $H_2S$, with the former also $SO_2$. When heat is applied, more rapid reactions are obtained. A cold alcoholic solution of picric acid does not alter the three colours. A cold and dilute alum solution evolves with the green colour sulphuretted hydrogen, the blue and violet appearing unaltered. After some time, however, the blue pigment evolves the same gas. A warm and concentrated solution rapidly decomposes the green and blue and only a boiling solution seems to affect the violet.

Although ultramarine gives up some of its sulphur to warm alkaline solutions, no change of colour could be noticed. An aqueous solution of caustic ammonia, soda, or potash does not act on the blue and green colours, but turns the violet colour blue. Very concentrated solutions attack the green and blue. Formic acid behaves like an ordinary acid. Aldehyde, sodium amalgam, and potassium amalgam in presence of water, a hot solution of sodium thiosulphate, thiosulphuric acid with excess of potash, a hot solution of potash and grape sugar, a warm dilute alcoholic or aqueous solution of potash with a stream of sulphuretted hydrogen, yellow ammonium sulphide, an alcoholic potash solution with pyrogallic acid or sulphur, &c., remained indifferent to the three ultramarines. A whole series of oxidising agents had no action. A boiling solution of silver nitrate attacks neither the green nor the violet, but gives the blue a dirty green colour. Fused silver nitrate attacks the ultramarines very strongly and turns them white. Bromine renders them colourless. Concentrated nitric acid decolorises the ultramarines with evolution of red vapours. At a moderately hot temperature the violet becomes blue, and at a higher temperature behaves like the blue. The blue becomes altered at a bright red heat, when it assumes a white colour. The green colour, after heating for some time, turns greenish-blue, and when heated to redness turns white. Various reducing substances turn the violet either yellow, violet, blue or else colourless. The blue is changed to either green or white, whereas the green behaves as if heated by itself. Carbonic oxide has no effect when heated with the blue and green colours, but turns the violet blue. A stream of hydrogen did not alter the blue; the violet turned blue and the green yellowish-brown. When heated with arsenious acid, the green remained unaltered, the blue formed a sublimate of arsenious sulphide and turned green, and the violet turned blue in the air, but green when the latter was excluded. On heating the green with metallic arsenic, it partly turned blue, partly orange-yellow, and partly formed a yellow sublimate;

the blue under the same conditions assumed a darker and dirty colour, but the violet remained unaltered. When heated with zinc-dust the three colours were decolorised. When heated with mercury in closed vessels, the green and violet are not altered, the blue turns darker. When they are treated similarly with carbon disulphide no reaction takes place, except solution of sulphur. When the green is heated with sulphur, with exclusion of air, it assumes a dark greenish-blue colour, but in the air it turns blue, while the violet turns bluish-violet and is partly converted into red. When heated in a stream of sulphurous acid the green turns violet, and in a stream of sulphuretted hydrogen the violet turns blue. When heated with charcoal, the green turns yellow, the blue evolves sulphurous acid without change of colour, the violet turns blue, or partly green, and if heated very strongly it turns white. When heated with sodium sulphide, the green turns grey and the violet blue; with sodium thiosulphate the violet turns blue, the green and blue not being altered. In the experiments with oxidising agents, some of the latter bodies changed the colour of the green at a moderately high temperature to a greenish-blue colour, whereas the blue resisted and the violet turned blue. At high temperatures the three colours turned white. When heated with arsenic acid to a slight redness, the green changes to a blue and at a higher temperature to a white. The blue and violet ultramarines are converted into a white. When heated with mercuric oxide, the green turns greenish-blue, the blue white, and the violet partly blue, partly rose-red, partly white, according to the temperature. When heated with ammonium nitrate, the violet turns blue, while the green and blue are not changed; at high temperatures, however, the latter turn white. If heated with potassium nitrate, the green turns to a lighter and bluish colour, the blue undergoes no change, and the violet assumes a greyish-green colour. Heated with potassium chlorate, the green turns darker and loses its brightness of colour, the blue remains unaltered, but the violet is converted into a fine blue. In oxygen at a moderate temperature, the green turns blue, the blue is not changed but evolves sulphurous acid, and the violet turns blue. Both the latter turn white if a strong heat is used. Mercuric chloride changes the violet to blue, the green at a dull red heat to blue, at a white heat to white, while the blue remains blue at a moderate heat, but turns white if heated very strongly. When heated to 140° with carbon tetrachloride in closed vessels, the green partly turns blue, partly gives a yellow solid; the violet partly turns red, partly white. The alkalis strongly attack the colours at high temperatures. The green and blue resist the action of borax, but the violet turns light blue. Sodium and ammonium phosphate alter the three colours, turning them white if heated strongly. Boiling water extracts from the blue and green ultramarines only very small quantities of calcium sulphate, but large quantities of the latter from the violet colour. Steaming does not affect the ultramarines; alteration of colour must be attributed to the action of steam on the thickening materials. By the decomposition of the three colours with hydrochloric acid various sulphur-compounds are formed. The violet gives most and the green least sulphuric acid, the violet gives also most sulphurous acid and the green least. The green gives least thiosulphuric acid, the blue only one-fifth of that of the

violet. The largest quantity of sulphuretted hydrogen is evolved from the green, the violet showing the least. The blue contains most and the green least free sulphur.

The authors are not yet able to say whether the various compounds of sulphur are in reality present in the ultramarines, or whether the sulphurous acid, free sulphur, &c., are merely states in which the sulphur exists at the moment of the decomposition of the colours by an acid.

With regard to the chemical formulæ of the three ultramarines no positive results have been obtained; but the various reactions and the quantitative analyses afford proof of the fact that each of the three colours has its separate composition. The most probable constitution seems to be that in which, in double silicates of aluminium and sodium, the oxygen is partly replaced by sulphur. Even if we could obtain the three colours chemically pure, an accurate determination of the molecular constitution, the placing of the atoms, and of the rational formulæ would be found very difficult, on account of the insolubility of the colours in the ordinary solvents, and on account of their behaviour to energetic reagents required to decompose them and to dissolve their constituents.

D. B.

**Behaviour of Vegetable and Animal Fibre during the Carbonisation of Wool and Cloth.** By J. WIESNER (Dingl. polyt. J., ccxx, 454—459).

THE ready and apparently complete destruction of the vegetable matter in the carbonising of wool and cloth induced the author to investigate this process experimentally. As a rule, dilute sulphuric acid is allowed to act on the wool at the ordinary temperature, after which the adhering liquid is removed mechanically—best by means of a centrifugal machine—the wet material is heated to 50°—100°, and the last traces of acid are washed out with water and soda. The wool does not suffer during this process, but the vegetable matter is almost completely destroyed.

Since the substances composing vegetable textures and organs behave differently to sulphuric acid, the author in the first place thought it necessary to study the behaviour of those substances which are present in wool. He found the foreign matters in most wools to consist of vegetable matter, with but mere traces of earth or small fragments of insects. He found in the vegetable matter (1) the fruits of the following plants:—*Xanthium spinosum*, *Echinospermum Lappula*, *Galium aparine*, *Medicago minima*, *Daucus Carota*. (2.) Particles of straw and grass. (3.) Coarse fibres of tissues. (4.) Fragments of leaves and stalks of herbs. To investigate the effects which carbonising produces on these vegetable matters, it was necessary to notice how the pure cellulose, the lignified cellulose, and that covered with a cuticle behave during this process. Swedish filter-paper was used in the place of pure cellulose, while for the lignified cellulose saw-dust of pitch-pine, and for that covered with a cuticle, raw cotton formed the substitutes. The following results were obtained:—Lignified vegetable

fibres became fragile and assumed a dark-brown colour when treated with a 1—2 p. c. sulphuric acid solution and heated to 50°. At 55° signs of coking were visible. Pure cellulose is somewhat more resistant. If treated with a 1—2 p. c. solution and heated to 50°—55°, it becomes fragile after the lapse of an hour; it turns brown at 60° and cokes at 65°. Cotton treated with the same solution becomes fragile at 60°—62°, turns brown at 70°—72°, and cokes some degrees over 72°.

What changes does the animal fibre undergo if subjected to the same process, by which the above-named vegetable substances are destroyed? To answer this question it was necessary to determine the absolute tenacity of the unaltered and of the carbonised animal fibre. The author experimented with the tail-hairs of horses (10—15 cm. long and 0·16 mm. in diameter). He determined the absolute tenacity of each separate hair by a direct tearing-test, and then subjected the longer end of the torn thread to various carbonising processes at different temperatures, &c., until a comparison sample of cotton was totally destroyed, when the absolute tenacity of the thread thus treated was again ascertained.

The following results were obtained:—1—5 p. c. sulphuric acid solution increased the absolute tenacity of the carbonised hair. 6 p. c. solution did not further alter it, but higher percentage solutions of acid decreased the tenacity. The increase of the absolute tenacity of animal hair in carbonising with an acid solution of low percentage and at not too high a temperature, probably depends upon the fact that the acid, without changing the substance of the fibre materially, brings the histological elements to a swollen condition, by which the tissue of the hair gains in density.

D. B.

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**Disinfectants.** (Dingl. polyt. J., ccxix, 375.—*Potassium permanganate* solution does not cause the death of infusoria for a long time. The spores of *Mucor* and *Penicillium* grow in strong solutions of this salt. Bacteria are killed by concentrated solution, but they increase in solution of 1·1000. When meat is placed in a solution of this salt, it is permeated with the liquid, but the action results in a decomposition of the permanganate, after which the meat is acted on by bacteria, &c. Permanganate may be advantageously employed for washing wounds; for disinfection of decaying matter it is, however, useless.

Dry *chlorine* is without action on the lower organisms; attempts to disinfect clothes, &c., by fumigation with chlorine are therefore useless.

*Phenol* quickly kills all lower organisms; it is, therefore, one of the best of all disinfectants.

*Heat* kills many of the lower organisms. Hot steam and water may become good disinfectants.

M. M. P. M.

# PAPERS READ BEFORE THE CHEMICAL SOCIETY.

## XXII.—*On the Slow Oxidation of Potassium.*

By SYDNEY LUPTON, M.A.

IN the Bakerian Lecture read before the Royal Society in 1807, Sir H. Davy (Works, vol v, p. 1) gives an account of some experiments made by passing oxygen over potassium heated in a silver boat placed in a glass tube.

The composition of the oxide thus obtained was found to be—

| | I. | II. |
|---|---|---|
| Potassium ..... | 86·7 | 85·5 |
| Oxygen ..... | 13·3 | 14·5 |

The oxide nearest to these results in composition is the protoxide $K_2O$,* which contains 83·03 per cent. of potassium.

The numbers obtained by Davy are as exact as could be expected, when we consider the small amount of potassium at his disposal, its probable impurity, and the considerable difficulty at that time of making an accurate analysis of such a body.

In the course of the next few years many researches on the oxides of potassium were made by Gay-Lussac and Thénard, by Berzelius, and by Davy himself. The results obtained are summed up by Berzelius in his *Traité de Chimie*, published in France in 1846.

A. Suboxide of potassium; prepared—

1. By heating potassium in air containing too little oxygen to convert it into oxide.

2. By heating below 300° 1 part of potassium with $1\frac{1}{5}$ parts of potash.

When hot, a red-grey solid; when cold, grey.

It was not analysed, but its composition was assumed to be $K_4O$ in the modern notation.

B. Oxide of potassium; prepared—

1. By burning potassium in the *right* amount of dry oxygen.

* The following atomic weights are used throughout:—

$$\left.\begin{array}{l} Na = 22{\cdot}98 \\ O = 15{\cdot}96 \\ K = 39{\cdot}04 \\ Cl = 35{\cdot}368 \\ N = 14{\cdot}009 \end{array}\right\} \text{Stas, } \textit{Nouv. Rec.}, \text{ p. 24.}$$

2. By heating 1 part of potassium with 1·4 parts of potash, when hydrogen is given off and 2·3 parts of anhydrous potash are formed.

The composition of this oxide was found to be—

| | |
|---|---|
| Potassium ..... | 83·05 |
| Oxygen ..... | 16·95 |

Hence its formula is $K_2O$, which requires 83·03 per cent. of potassium.

C. Gay-Lussac and Thénard's peroxide of potassium; prepared—

1. By burning potassium in oxygen.

2. By heating potassium with fused nitre.

The best results obtained by Gay-Lussac and Thénard give for the composition of this oxide:

| | |
|---|---|
| Potassium ..... | 62·02 |
| Oxygen ..... | 37·98 |

This result agrees very nearly with potassium trioxide, $K_2O_3$, which contains 61·99 per cent. of potassium.

The matter remained in this state for many years, until the publication of a valuable paper by Harcourt (*Chem. Soc. J.*, xiv, 267), to which I cannot do better than refer for a further account of the literature of the subject.

The method employed by Harcourt consisted in submitting potassium heated in a flask to temperatures from 100 to 280° C. to the action of air and oxygen. The flask was weighed before and after each of the operations, and thus the weight of oxygen, which had entered into combination with the known weight of potassium, was determined.

The existence of a dioxide, $K_2O_2$, was thus rendered probable, and that of a tetroxide, $K_2O_4$, certain; while some doubt was thrown on the existence of the trioxide, $K_2O_3$.

The dioxide was only analysed volumetrically, but the composition of the tetroxide was determined by four different methods:—

1. The potassium was estimated as sulphate by weight or by titration.

2. The oxygen evolved by contact with water and platinum-black was measured.

3. The oxygen evolved by contact with acidulated water was measured.

4. The amount of active oxygen in the solution of the oxide was determined by permanganate.

To sum up these results, the following oxides of potassium have been proved or supposed to exist:—

$K_4O$.
$K_2O$, Davy and Berzelius.
$K_2O_2$, Harcourt.
$K_2O_3$, Gay-Lussac and Thénard.
$K_2O_4$, Harcourt.

Notwithstanding the number and accuracy of the experiments of which a brief account has been given, there still seemed to be some few points left in doubt, well worthy of further investigation.

The dioxide had not been obtained in a solid condition, and analyses both of it and of the trioxide were required to confirm the results of Harcourt and of Gay-Lussac and Thénard.

Further, the composition $K_4O$ assigned to the blue-grey oxide of potassium necessitated the tetratomicity of oxygen; which, however probable from theoretical considerations, is a question well worthy of determination by direct experiment. The formula $K_4O$ was probably given to this oxide from its supposed analogy to the suboxide of silver $Ag_4O$, on the existence of which, however, considerable doubt is thrown by Fairley's recent researches.

The first oxidizing agent used was a mixture of air and nitrogen, which, however, was found to present no greater advantages than dry air. Nitrous oxide was also used for several experiments.

The potassium was purified by Harcourt's filtration method, and oxidized in a small flask placed in a water-bath. The flask was of hard Bohemian glass with a greenish tint, and was found to be quite unacted upon, one flask serving for all the experiments.

Some difficulty was found in obtaining a satisfactory method of analysis (synthetical determinations were useless, as will hereafter be seen); the following method was found sufficiently accurate, and was used in every instance.

The oxide was kept over oil of vitriol in a glass tube closed with a caoutchouc bung. It was weighed by difference ($w_1$) into an ignited and weighed Berlin crucible.

The crucible containing the oxide was then placed uncovered on a moistened glass plate, and over it was placed an inverted beaker tilted to allow access of air. The oxide was thus in the course of a few hours converted, without spitting, into a mixture of hydrate and carbonate; a few c.c. of water and excess of dilute hydrogen chloride were added, and the contents of the crucible evaporated to dryness on the water-bath.

The crucible being now covered was gently heated for some time and then ignited to low redness; after cooling, the crucible and its contents were weighed. The difference between this last weight and the original weight of the crucible gave ($w_2$) the weight of potassium chloride formed.

If $x$ be the percentage of potassium in any sample of oxide,

$$\text{Log. } x = 1{\cdot}7198902 + \log. w_2 - \log. w_1.$$

The advantages of this method are: that all spitting of the oxide is avoided; that exposure of the oxide between the weighings is reduced to a minimum; that the method does not require close attention during its whole course; that the difficulty with the acid sulphate of potassium incidental to the use of hydrogen sulphate is avoided; and, finally, that all the atomic weights entering into the calculation have been carefully determined.

The following experiments were made to test the correctness of the results obtainable by this method of analysis. The potassium was determined in a sample of normal potassium carbonate prepared from cream of tartar:—

| | | |
|---|---|---|
| (*a.*) | Weight of potassium carbonate taken.... | 0·1715 |
| | Weight of potassium chloride formed.... | 0·184 |
| | $\therefore x = 56{\cdot}29$ per cent. of potassium. | |
| (*b.*) | Weight of potassium carbonate taken .... | 0·1925 |
| | Weight of potassium chloride formed.... | 0·2065 |
| | $\therefore x = 56{\cdot}28$ per cent. of potassium. | |
| (*c.*) | Weight of potassium carbonate taken .... | 0·2525 |
| | Weight of potassium chloride formed .... | 0·271 |
| | $\therefore x = 56{\cdot}31$ per cent. of potassium. | |

| | | | | | |
|---|---|---|---|---|---|
| $K_2$ ..... | = 78·08 | 56·6 | 56·29 | 56·28 | 56·31 |
| $CO_3$..... | = 59·88 | 43·4 | — | — | — |
| | 137·96 | 100·0 | | | |

These results, though not so high as theory requires, probably from the presence of traces of tartaric, and a slight excess of carbonic acid, show a satisfactory concordance among themselves.

Two samples of sodium carbonate, also prepared from the tartrate, were next analysed; the sample which gave *a* and *b* had been some years longer in stock than that which gave *c* and *d*. Both samples contained a small amount of tartaric acid.

If $y$ be the percentage of sodium present in the carbonate,

$$\text{Log. } y = 1{\cdot}5953240 + \log. w_2 - \log. w_1.$$

Sodium chloride requires to be dried with still greater care than potassium chloride, since the crystals formed under similar conditions are considerably larger.

| | | |
|---|---|---|
| (*a.*) | Weight of sodium carbonate taken ..... | 0·2459 |
| | Weight of sodium chloride formed ..... | 0·2702 |
| | $\therefore y = 43{\cdot}28$ per cent. of sodium. | |

(*b.*) Weight of sodium carbonate taken ..... 0·2321
Weight of sodium chloride formed ..... 0·2548
$\therefore y = 43{\cdot}24$ per cent. of sodium.

(*c.*) Weight of sodium carbonate taken ..... 0·27285
Weight of sodium chloride formed ..... 0·3004
$\therefore y = 43{\cdot}36$ per cent. of sodium.

(*d.*) Weight of sodium carbonate taken ..... 0·5785
Weight of sodium chloride formed ..... 0·63675
$\therefore y = 43{\cdot}35$ per cent. of sodium.

| | | | | *a.* | *b.* | *c.* | *d.* |
|---|---|---|---|---|---|---|---|
| $Na_2$ | = | 45·96 | 43·42 | 43·28 | 43·24 | 43·36 | 43·35 |
| $CO_3$ | = | 59·88 | 56·58 | — | — | — | — |
| | | 105·84 | 100·00 | | | | |

These results are too low, for the same reasons as those assigned in the case of the potassium carbonate.

The general result of these seven experiments seems to be that this method of analysis is quite sufficiently accurate to determine which of two formulæ for an oxide of potassium is the right one, even in the case of a compound containing many atoms, both of potassium and of oxygen.

Let us first consider the oxidation of potassium by dry air at temperatures below 100° C. The more thoroughly the air is dried, the less is its oxidizing action: hence the air was passed over and through a considerable surface and volume of oil of vitriol.

It was found that a temperature of about 65° sufficed to commence the oxidation, which would then continue in summer without any external aid, but in winter the water-bath must be slightly warmed. The exfoliation took place in an exactly similar manner to that observed by Harcourt (*loc. cit.*)

After about six hours' oxidation, the product is a greenish powder with larger blue and yellow lumps interspersed; on two occasions some of the blue lumps were picked out and analysed.

A. First oxidation:

(*a.*) Weight of blue oxide taken ..... 0·1119
Weight of chloride formed ..... 0·1709
$\therefore x = 80{\cdot}1$.

(*b.*) Weight of blue oxide taken ..... 0·1121
Weight of chloride formed ..... 0·1706
$\therefore x = 79{\cdot}8$.

B. Second oxidation:

(*c.*) Weight of blue oxide taken ..... 0·16
Weight of chloride formed ..... 0·2425
$\therefore x = 79·5$.

(*d.*) Weight of blue oxide taken ..... 0·29
Weight of chloride formed ..... 0·4384
$\therefore x = 79·3$.

The oxide of potassium which approaches most nearly in composition to these results is represented by $K_8O_5 = 3K_2O + K_2O_2$.

| | | | | *a.* | *b.* | *c.* | *d.* |
|---|---|---|---|---|---|---|---|
| $K_8$ | = | 312·32 | 79·65 | 80·1 | 79·8 | 79·5 | 79·3 |
| $O_5$ | = | 79·8 | 20·35 | — | — | — | — |
| | | 392·12 | 100·00 | | | | |

Though these results are not very concordant, they agree fairly well with the calculated percentage, and show that this oxide differs much in composition from the suboxide $K_4O$, which contains 90·73 per cent. of potassium.

After continuing the passage of the air for six hours longer on two separate occasions, blue lumps were picked out and analysed.

(*a.*) Weight of blue oxide taken ..... 0·1933
Weight of chloride formed ..... 0·282
$\therefore x = 76·54$.

(*b.*) Weight of blue oxide taken ..... 0·2245
Weight of chloride formed ..... 0·3275
$\therefore x = 76·54$.

These numbers are almost identical with those required by $K_4O_3 = K_2O + K_2O_2$.

| | | | | *a.* | *b.* |
|---|---|---|---|---|---|
| $K_4$ | = | 156·16 | 76·534 | 76·54 | 76·54 |
| $O_3$ | = | 47·88 | 23·466 | — | — |
| | | 204·04 | 100·000 | | |

For convenience a result may now be mentioned which was obtained at a further stage of the inquiry. After passing nitrous oxide at a temperature of 80—90°, instead of air, blue lumps were also obtained; one of these was picked out and analysed.

Weight of blue oxide taken ..... 0·0941
Weight of chloride formed ..... 0·1405
$\therefore x = 78·34$.

The oxide nearest to this result in composition is expressed by the formula $K_6O_4 = 2K_2O + K_2O_2$.

| | | | |
|---|---|---|---|
| $K_6$ = | 234·34 | 78·58 | 78·34 |
| $O_4$ = | 63·84 | 21·42 | — |
| | 298·18 | 100·00 | |

From these results it seems probable, that the blue oxide which forms on a freshly-cut surface of potassium is not a suboxide, as is generally supposed, but one of several molecular combinations of the protoxide and dioxide of potassium.

Some confirmation of the analytical results obtained for these oxides is afforded by the fact that one of them, when thrown into water, gives off oxygen and not hydrogen, which might be expected from the suboxide—

$$K_4O_3 + 2H_2O = 4HKO + O$$
$$K_4O + 3H_2O = 4HKO + H_2.$$

These experiments also seem to throw very great doubt on the composition of the grey oxide mentioned by Berzelius—the first method of preparation would give one of these oxides and free potassium, the second, probably potash with some free potassium; more especially since I have found that free potassium may exist, particularly when coated with oxide, in presence of all except, possibly, the tetroxide of potassium.

It may be worth while to compare these oxides of potassium, *i.e.*—

$$K_2O$$
$$K_8O_5 = 3K_2O + K_2O_2$$
$$K_6O_4 = 2K_2O + K_2O_2$$
$$K_4O_3 = K_2O + K_2O_2$$
$$K_2O_2,$$

with the various intermediate oxides of lead, many, if not all of which, may be obtained by passing air over heated lead—

$$PbO$$
$$Pb_6O_7 = 5PbO + PbO_2 \text{ (Longchamps)}$$
$$Pb_4O_5 = 3PbO + PbO_2 \text{ (Labillardière)}$$
$$Pb_3O_4 = 2PbO + PbO_2 \text{ (Dumas)}$$
$$Pb_2O_3 = PbO + PbO_2 \text{ (Winkelblech)}$$
$$PbO_2.$$

(c.f. Mulder, *J. für prakt. Chem.*, i, 438.)

The intermediate oxides of molybdenum may also be mentioned—

$$MoO\,?$$
$$Mo_2O_3 = MoO + MoO_2$$
$$MoO_2$$

$$Mo_2O_5 = MoO_2 + MoO_3$$
$$Mo_3O_8 = MoO_3 + 2MoO_3$$
$$MoO_3.$$

(c.f. Rammelsberg, *Pogg. Ann.*, cxxvii, 381.)

The oxides of lead are the more remarkable since the oxidation seems to be continuous, *i.e.*, one oxide passes into another by a longer exposure to the same conditions.

One of the yellow lumps was also picked out from the greenish mixture and analysed.

| | |
|---|---|
| Weight of yellow oxide taken ..... | 0·192 |
| Weight of chloride formed..... | 0·2558 |

$\therefore x = 69·9$ per cent. of potassium.

Hence this is probably the dioxide with a small mixture of one of the higher oxides, the dioxide passing to a higher stage of oxidation before the whole mass has passed into dioxide.

Harcourt has shown (*loc. cit.*) that the tetroxide may be fused without decomposition. It seemed, therefore, worth while to try the effect of fusion on the greenish mixture.

The first difficulty, which has not yet been overcome, was to find some substance unacted on by the fused oxide.

A quantity of the yellowish-green mixture of oxides was prepared and analysed; the sample *a* being taken before and *b* after the succeeding experiments.

| | | |
|---|---|---|
| (*a.*) | Weight of oxide taken ..... | 0·431 |
| | Weight of chloride formed ..... | 0·6033 |

$\therefore x = 73·4$ per cent. of potassium.

| | | |
|---|---|---|
| (*b.*) | Weight of oxide taken ..... | 0·1797 |
| | Weight of chloride formed ..... | 0·2523 |

$\therefore x = 73·6$ per cent. of potassium.

These results are rather higher than those required for potassium dioxide.

The two following experiments were made with this sample of oxide:—

(*a.*) 0·712 gram was fused in a Berlin crucible. The reddish-brown fluid on cooling formed a yellow mass, which, on analysis, gave 0·966 gram of chloride $\therefore x = 71·18$ per cent. of potassium.

(*b.*) 0·446 gram of oxide gave, after fusion, 0·6017 gram chloride. $\therefore x = 70·78$ per cent. of potassium.

| | | | *a.* | *b.* | Mean. |
|---|---|---|---|---|---|
| $K_2$ = | 78·08 | 70·98 | 71·18 | 70·78 | 70·98 |
| $O_2$ = | 31·92 | 29·02 | — | — | — |
| | 110·00 | 100·00 | | | |

Since, according to Harcourt, silver is acted on by fused potassium tetroxide, and the Berlin crucible was somewhat attacked during the last two experiments, a platinum crucible, lined with gold, was used for the next two.

*a.* 0·3032 gram of the green mixture of oxides was gently fused in the gold-lined crucible; after fusion, the oxide weighed 0·33025 gram. During the fusion, the crucible was evidently attacked, brown-black auric oxide being formed; the loss of weight of the crucible during the experiment amounted to 0·00165 gram.

Hence $x$ = 72·2 per cent. of potassium before fusion.
$x_1$ = 66·3 „ „ after „

*b.* In this experiment, the oxide was somewhat more oxidized, and the fusion was continued for a shorter time.

| | |
|---|---|
| Weight of oxide taken before fusion..... | 0·3688 |
| „ „ „ after „ ..... | 0·3832 |
| „ of chloride formed..... | 0·4995 |
| Loss of weight of crucible during experiment.... | 0·0004 |

∴ $x$ = 71·05 per cent. of potassium before fusion.
$x_1$ = 68·5 „ „ after „

It is needless to call special attention to the oxidation of the gold; but it seems curious that the oxidation should take place much more rapidly in a gold than in a porcelain crucible; when, from the action of hydrogen dioxide on auric salts, a contrary result might have been expected.

Before proceeding further, it may be worth while to mention four reactions of the yellow-green mixture of oxides:—

A. When this mixture was thrown into a mixture of hydrogen chloride and sulphite, some sulphate is formed.

B. When it is thrown into absolute alcohol (methylated), gas is evolved, and a yellow flaky precipitate falls, which is very slowly dissolved by the alcohol.

C. When the green mixture of oxides is heated in a boat of gas-coke in a current of nitrogen, the powder turns through yellow to orange-red. At the moment of fusion, ignition takes place, with formation of potassium carbonate and a brilliant mirror of metallic potassium forms on the tube—

$$3K_2O_2 + C_2 = 2K_2CO_3 + K_2.$$

D. When the mixture of oxides is heated in a current of dry nitrogen in a porcelain boat lined with magnesia, the oxides turn orange-red and viscous. On raising the temperature slightly, fusion takes place; but at the moment of fusion, the mass glows, a rapid evolution

of oxygen takes place, and the colour changes to faint yellowish-white, even while hot.

This result seems to be due to the formation and instantaneous decomposition of magnesium dioxide, as yet unknown—

$$K_2O_2 + MgO = K_2O + MgO_2$$
$$MgO_2 = MgO + O.$$

On throwing the white residue into water, no evolution of gas took place—

$$K_2O + H_2O = 2HKO.$$

This reaction might possibly afford another and more convenient method for the preparation of potassium monoxide.

Acting on a suggestion for which I am indebted to Mr. Harcourt, I used in the following experiment nitrous oxide, prepared from pure ammonium nitrate, and passed through ferrous sulphate, instead of air, as the oxidizing agent.

The phenomena observed were exactly similar to those when air was used. The formation and analysis of a blue oxide has already been mentioned; on longer heating, a brownish-yellow oxide was obtained, three samples of which were analysed.

| | | |
|---|---|---|
| (*a.*) | Weight of brown-yellow oxide taken ..... | 0·2257 |
| | Weight of chloride formed..... | 0·29905 |
| | $\therefore x = 69·53$ per cent. of potassium. | |
| (*b.*) | Weight of brown-yellow oxide taken ..... | 0·3772 |
| | Weight of chloride formed..... ... | 0·5003 |
| | $\therefore x = 69·57$ per cent. of potassium. | |
| (*c.*) | Weight of brown-yellow oxide taken ..... | 0·2562 |
| | Weight of chloride formed..... | 0·3401 |
| | $\therefore x = 69·65$ per cent. of potassium. | |

*c.* contained a trace of blue oxide.

| | | | *a.* | *b.* | *c.* |
|---|---|---|---|---|---|
| $K_2$ | = | 70·98 | 69·53 | 69·57 | 69·65 |
| $O_2$ | = | 29·02 | — | — | — |
| | | 100·00 | | | |

The fact that these results are somewhat too low may possibly be due to imperfect desiccation of the nitrous oxide. The last traces of moisture, which seem to be very difficult to remove from nitrous oxide, would probably exert a strongly oxidizing power.

On the other hand, as in the case of air, the oxidizing action of nitrous oxide may be continuous.

Though these results are far from being as concordant as might be

desired, still when taken in connection with others that have been mentioned, they seem, on the whole, to leave no doubt of the existence of the dioxide $K_2O_2$ in the solid state. The experiments of Harcourt have shown this oxide to exist in aqueous solution.

It has long been known that potassium burns readily in nitrogen tetroxide with a reddish flame (c.f. Gmelin, ii, 384).

The oxide formed, which is white even while hot, seems not to have been analysed; it seems probable, from its colour, that it is pure potassium monoxide, $K_2O$, but the point is worthy of further investigation.

Another possible method for the formation of one or more oxides of potassium, was suggested by the following statement of Gmelin, iii, 69:—

"At a red heat (potassium nitrate) evolves oxygen gas at first tolerably pure, but afterwards contaminated with a constantly increasing quantity of nitrogen, and is thereby converted first into nitrite, and then into pure potash and peroxide of potassium."

A quantity of pure potassium nitrate was powdered and dried for some time on the water-bath—

0·451 gram of the pure dry potassium nitrate, fused with excess of previously ignited potassium dichromate, lost 0·24095 gram, or 53·42 per cent.

| | | |
|---|---|---|
| $K_2O$ = | 46·586 | |
| $N_2O_5$ = | 53·414..... | 53·42 |
| | 100·000 | |

Hence this sample of potassium nitrate seemed pure within the errors of experiment.

(*a.*) 0·7447 gram of potassium nitrate was heated for 1½ hours to bright redness in a Berlin crucible. Whitish fumes were given off, and the fluid turned yellowish. The white mass, on cooling, had lost 0·1029 gram, or 14 per cent. Its solution in water was slightly alkaline to litmus, and gave nitrous fumes on the addition of dilute hydrogen sulphate.

(*b.*) 0·86 gram of potassium nitrate, heated to intense redness over a gas blowpipe for half-an-hour, lost 0·42 gram, or 49·8 per cent. On treatment with dilute acid, the residual mass still gave nitrous fumes.

Since these results seemed to differ from Gmelin's statement, an attempt was made to reduce the nitrate by heating it with magnesia.

(*c.*) 0·625 gram of potassium nitrate and 0·2502 gram of freshly ignited magnesia were heated to redness for 1½ hours; the loss was 0·1 gram, or 16 per cent., nearly corresponding to 1 atom of oxygen. On further heating to intense redness over the blowpipe for three-

quarters of an hour, the total loss amounted to 0·22 gram, or 35·2 per cent.

(*d.*) 0·8396 gram of potassium nitrate and 0·6339 gram of magnesia, after ignition to intense redness for two hours, lost 0·3125 gram, or 37·2 per cent. The residue was white and gave off no nitrous fumes on the addition of an acid.

Though these results are far from concordant, they seem to show that the extreme heat required to expel the last traces of nitrous compounds precludes any hope of obtaining a definite oxide of potassium by this method.

When the yellow-green mixture of oxides is exposed to air containing moisture, a curious series of reactions seems to take place, the more rapidly the warmer and moister the air may be.

The yellow-green mixture used corresponded nearly in composition with the dioxide, since it contained about 73 per cent. of potassium.

A. A portion of the yellow-green mixture was exposed to the air in an uncorked tube; the greenish mixture gradually turned to a pale lemon-yellow.

(*a.*) Weight of yellow oxide taken ..... 0·2953
Weight of chloride formed ..... 0·3457
$\therefore x = 61·4$ per cent. of potassium.

(*b.*) Another sample after shorter exposure.
Weight of yellow oxide taken ..... 0·3666
Weight of chloride formed ..... 0·4375
$\therefore x = 62·6$ per cent. of potassium.

B. The oxide was exposed to air at a rather lower temperature and partially dried by oil of vitriol.

(*c.*) After three days' exposure the oxide turned lemon-yellow.
Weight of yellow oxide taken ..... 0·7012
Weight of chloride formed ..... 0·8223
$\therefore x = 71·53$ per cent. of potassium.

(*d.*) After 14 days' exposure the oxide had deepened in colour.
Weight of yellow oxide taken ..... 0·313
Weight of chloride formed ..... 0·3227
$\therefore x = 54·1$ per cent. of potassium.

(*e.*) After 21 days' exposure the oxide had become lighter in colour.
Weight of yellow oxide taken ..... 0·3079
Weight of chloride formed ..... 0·365
$\therefore x = 62·2$ per cent. of potassium.

C. Another sample of the mixed oxides was exposed.

(*f.*) Weight of yellow oxide taken ..... 0·2656
Weight of chloride formed ..... 0·319
$\therefore x = 63$ per cent of potassium.

(*g.*) After a longer exposure.
Weight of yellow oxide taken ..... 0·6646
Weight of chloride formed ..... 0·7422
$\therefore x = 58·6$ per cent. of potassium.

D. (*h.*) Another sample of the mixed oxides was exposed for some time.
Weight of yellow oxide taken ..... 0·183
Weight of chloride formed ..... 0·1944
$\therefore x = 55·7$ per cent. of potassium.

These numbers may be compared with those required by the tri- and tetroxide of potassium.

| | | | *a.* | *b.* | *c.* | *e.* | *f.* |
|---|---|---|---|---|---|---|---|
| $K_2$ = | 78·08 | 61·99 | 61·4 | 62·6 | 61·53 | 62·2 | 63 |
| $O_3$ = | 47·88 | 38·01 | — | — | — | — | — |
| | 125·96 | 100·00 | | | | | |

| | | | *d.* | *g.* | *h.* |
|---|---|---|---|---|---|
| $K_2$ = | 78·08 | 55·02 | 54·1 | 58·6 | 55·7 |
| $O_4$ = | 63·84 | 44·98 | — | — | — |
| | 141·92 | 100·00 | | | |

It is needless to point out the difficulties which beset any attempt to obtain accurate numbers by such a method as the one we are now considering. The colour is the only test we at present have for homogeneity. Nevertheless it seems at least probable that by the action of moist air the lower oxides of potassium pass to the lemon-yellow trioxide, then to the sulphur-yellow tetroxide, next back again to the trioxide, and finally to hydrate.

It seems possible that at some definite temperature and degree of saturation of the atmosphere (obtainable by exposing the oxide over definite mixtures of water and sulphuric acid: Regnault, *Ann. de Chimie et de Physique*, III, xv, 179), the trioxide might be obtained accurately and with certainty.

Finally the change of colour through which potassium passes when it is gradually oxidized may be noticed. The protoxide is white, the intermediate oxides grey-blue, the dioxide brownish-yellow, the trioxide lemon-yellow, and the tetroxide sulphur-yellow. When fused the di-, tri-, and tetroxide form deep orange-red masses turning nearly black as the temperature rises, but returning to yellow on solidifying. The

monoxide, as far as I know, has not yet been fused; it remains white even when intensely heated. The blue intermediate oxides fuse to a deep red fluid, but absorb oxygen more rapidly.

## XXIII.—*On Acetyl- and Nitro-derivatives of Alizarin.*

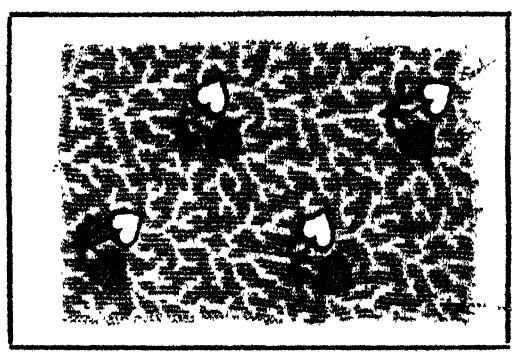
By W. H. Perkin, F.R.S.

In a paper read before the Society a few years since on anthrapurpurin (*Jour. Chem. Soc.*, xxvi, 430), I stated that triacetyl-anthrapurpurin and also diacetyl-alizarin, when subjected to the influence of nitric acid, produced derivatives which, when dissolved in potash and precipitated with an acid, gave colouring matters dyeing mordants shades of colour differing from those produced by anthrapurpurin and alizarin. Being desirous of determining the nature of these substances, I directed my attention to the alizarin derivative as being the easiest to prepare, and now beg leave to lay the following results before the Society:—

Diacetyl-alizarin was first obtained by Herr Schrodter. In a paper on anthraflavic acid I also gave an account of its preparation and properties (*Jour. Chem. Soc.*, xxvi, 21). It was originally prepared by heating alizarin and acetic anhydride in sealed tubes. As I was likely to require considerable quantities for my experiments, I endeavoured to dispense with sealed tubes, and found that by simply boiling alizarin with a considerable excess of acetic anhydride, the alizarin was changed into this body, an intermediate product, however, being first formed, to which I will now refer.

On boiling alizarin for several hours with acetic anhydride in excess, it was gradually acted upon, and after a time the mixture became a crystalline mass; the boiling was continued for about a day, so that no unchanged alizarin might remain, and the product then allowed to crystallise. The crystals were collected on a cloth filter, drained and pressed to remove acetic anhydride, and dissolved in boiling benzol. As the solution cooled, bright golden scales were deposited, but afterwards groups of primrose-yellow crystals. By watching the crystallisation and pouring off the mother-liquor as soon as the latter crystals began to form, the two bodies could be separated. The body which was first deposited was recrystallised several times from benzol, and gave the following numbers on analysis:—

·2855 of substance gave
·7165 of $CO_2$ and
·094 of $H_2O$.



NITROALIZARIN.

| Theory for $C_{14}H_6O_2\left\{\begin{matrix}(C_2H_3O)O\\HO\end{matrix}\right.$. | | Experiment. |
|---|---|---|
| Carbon ..... | 68·08 | 68·44 |
| Hydrogen ..... | 3·54 | 3·60 |

This substance is, therefore, monacetyl-alizarin. It differs from the diacetyl-derivative in crystallising in golden scales instead of primrose-yellow needles. It is less soluble in solvents, and fuses at a much higher temperature.

Both acetyl derivatives are decomposed with cold aqueous potash.

From the foregoing remarks it is evident that, to produce the diacetyl-derivative, it is only necessary to boil the mixture of alizarin and acetic anhydride for a long time; I have found two or three days sufficient, after which the product was allowed to cool, when it became a nearly solid mass of crystals. It was purified by pressure in a cloth filter, and then by crystallisation from benzol; in this manner considerable quantities were prepared.

### *Nitroalizarin.*

Diacetyl-alizarin, in fine powder, was gradually added to nitric acid, specific gravity 1·5, cooled with ice; it dissolved, and the acid became of the colour of bromine. This solution, when added to a large excess of water, deposited a yellow precipitate, which was collected, well washed with cold water, and when free from acid, boiled in water, to dissolve out a small quantity of an orange-coloured secondary product. The insoluble residue was dissolved in hot dilute caustic potash, with which it formed a blue-violet solution, and was then acidified with hydrochloric acid, when a copious yellow precipitate separated; this was washed, dried, and crystallised several times from alcohol. The yield of new product thus obtained was not, however, large.

In a second experiment the nitric acid was cooled with ice and salt; in this case scarcely any reaction took place, and on throwing the acid mixture into water, the precipitated product was found to be chiefly monacetyl-alizarin, the diacetyl-alizarin having lost half of its acetyl, apparently by the action of the water.

By working slowly at the ordinary temperature a somewhat better yield was obtained.

The new product gave on analysis the following numbers, which show it to be a mononitro-alizarin :—

I. ·302 of substance gave
·654 of $CO_2$ and
·071 of water.

II. ·426 of substance gave
·918 of $CO_2$ and
·101 of water.

III. ·243 gave
11 c.c. of N at 18° C., and 772 mm. bar.

| Theory for $C_{14}H_7(NO_2)O_4$. | | Experiment I. | II. | III. |
|---|---|---|---|---|
| Carbon..... | 58·94 | 59·03 | 58·77 | — |
| Hydrogen .. | 2·45 | 2·60 | 2·63 | — |
| Nitrogen .... | 4·91 | — | — | 5·28 |

Nitroalizarin crystallises from alcohol or glacial acetic acid in beautiful golden-yellow needles. It is not very soluble in either of these solvents, but of the two, least in glacial acetic acid. It is slightly soluble in water. It dissolves in caustic alkali with a very blue-violet colour, if anything bluer than that of alizarin; but if only a minute quantity of alkali is employed, the solution is of a beautiful crimson colour.

When its alkaline solution is examined by the spectroscope, it gives two bands similar to those of alizarin. These are best seen when an alcoholic solution is used; in both cases they are much less marked than those of alizarin. It dissolves in sodium carbonate, forming a violet solution if in excess, but crimson if in small quantities.

Its solution in ammonia is also violet.

When oxidized with nitric acid it produces a crystalline acid, which is apparently phthalic acid.

*Amido-alizarin.*

Nitroalizarin is rapidly changed under the influence of reducing agents. This is easily seen by boiling its potassic solution with granulated tin, when its blue colour quickly changes to a beautiful red, after which it becomes orange-red.

In studying this reaction, I have generally used sodium amalgam and an alkaline solution of nitroalizarin. On agitating the mixture for a few minutes the reaction is complete. This is seen by the liquid becoming of a clear bright red colour. As soon as this occurs, it is separated from the sodium amalgam (otherwise a second product is formed) and acidified, which causes the new product to separate as a dark chocolate powder; this, when washed with water and then dissolved in boiling alcohol, separates on cooling in small needles of a very black colour, but possessing a slight greenish metallic reflection.

On analysis it gave the following numbers:—

I. ·310 of substance gave
·750 of $CO_2$ and
·106 of $H_2O$.

II. ·308 of substance gave
·740 of $CO_2$ and
·103 of $H_2O$.

| Theory for $C_{14}H_7(NH_2)O_4$. | | Experiment. I. | Experiment. II. |
|---|---|---|---|
| Carbon ..... | 65·88 | 65·96 | 65·50 |
| Hydrogen ..... | 3·53 | 3·77 | 3·71 |

This product is therefore *amidalizarin*. It dissolves in alcohol, but not very freely, producing a beautiful crimson solution slightly fluorescent; alkalis likewise dissolve it, forming crimson solutions. It does not appear to form derivatives with acids; nitric acid quickly decomposes it. When boiled with sulphate of aluminia, it gives a beautiful purple solution from which ammonia precipitates a purple-red lake.

Its alcoholic solution, when viewed with the spectroscope, gives two bands, and perhaps a third faint one about F; the first is a little past D and the second near to E. The addition of a little alcoholic potash intensifies these two bands greatly.

Amidalizarin is also produced by another and somewhat remarkable reaction. When nitroalizarin is heated with concentrated sulphuric acid somewhat strongly, sulphurous acid is evolved, and on diluting the acid solution, amido-purpurin is precipitated. The product obtained by this means was not analysed, but it was found to contain nitrogen, to give the characteristic bands when examined by the spectroscope, and to dye mordants the colours peculiar to this substance.

It has been observed already that, if the action of nascent hydrogen on nitroalizarin be continued after amidalizarin is formed, a new product results. This substance is under examination. It contains nitrogen, dissolves in alkalis with an orange-red colour, and sublimes, forming a brownish-red sublimate.

*Dyeing Properties of Nitro- and Amidalizarin.*

These colouring matters possess the power of dyeing ordinary madder mordants. Nitroalizarin gives with alumina mordants very clear orange-red colours, not unlike some of the colours produced with aurine, and with iron mordants reddish-purple colours. The use of a small percentage of calcic carbonate in the dye-bath is very useful in dyeing with this substance.

Amidalizarin gives with alumina mordants purple colours, and with iron a bluish or steel-like colour.

These colouring matters also dye silk without the use of mordants, the former giving a golden-yellow and the latter a good crimson colour.

## XXIV.—*Educts from Baphia Nitida (Barwood).*

By (the late) THOMAS ANDERSON, M.D., F.R.S.E. Communicated by EDMUND J. MILLS, D.Sc., F.R.S.

THE wood, after having been torn to a fine dust, is placed in a digesting apparatus, and exhausted thoroughly with anhydrous "methylated" ether free from alcohol. The liquid which traverses the wood gradually diminishes in colour as the extraction proceeds, until, from having been strongly red, it becomes almost (though never quite) colourless. This liquid is heated in the water-bath, so as to drive off the greater part of the ether. The residue is left to itself for a short time in a cool place; it may deposit a small quantity of *baphic acid*, in the form of platy crystals. These are separated from the mother-liquid, in which they are quite insoluble; the latter is evaporated so as to drive off the greater part of the ether, and then mixed with alcohol. After an interval varying from one to several days, a crystalline magma forms; this consists of *baphiin*, contaminated with a solid red colouring matter, and containing besides some dark and viscous tinctorial substance which has not been examined.

After thoroughly drying off the ether from the wood used in the experiment referred to in the preceding paragraph, exhaustion with alcohol may be commenced. The alcoholic fluid is distilled to nearly dryness, and left to itself. It solidifies after long standing, to a semi-crystalline mass, containing (as in the case of the ethereal extract) a viscous colouring matter of a deep red colour. The mass, on exposure to air, dries up, with fission, into a granular powder. Its crystalline constituent has not been examined.

The use of other solvents than those above mentioned is not satisfactory. Benzol and carbonic sulphide have both been employed at about 100° C. They have the advantage of dissolving scarcely a trace of the colouring matters, but, on the other hand, the disadvantage of extracting a very trifling quantity of the colourless ingredient existing in the wood, to which the term baphiin has been applied. But should there be any baphic acid present, this is removed by the hot benzol with tolerable facility.

### *Baphiin*

Is obtained, as mentioned above, from the ethereal extract of the wood. In order to free it from colouring matter, it is repeatedly crystallised from strong spirit, whereby it is at length obtained perfectly pure. Baphiin is a colourless substance; it crystallises from

alcohol in plates of considerable lustre,—from ether, by rapid evaporation, in tufts of needles. It is only very sparingly soluble in benzol or carbonic sulphide; in water it is insoluble. When allowed to crystallise from its solution in alcohol on a finely divided surface in presence of air, it rapidly oxidises, producing colours which vary from yellowish-red to light purple. It has an odour of orris root. When submitted to the action of heat, baphiin fuses, but only in part, below 200°; in part at a higher temperature. This is an obvious sign of decomposition. At 100° it remains unchanged. Dried at the latter temperature it yielded on analysis the following results:—

| | Subs. | Carb. dioxide. | Water. | Carbon. | Hydrogen. | $C_{12}H_{10}O_4$. |
|---|---|---|---|---|---|---|
| (1.) | ·5340 gram. | 1·2974 | ·2278 | 66·26 | 4·74 | |
| (2.) | ·3251 gram. | ·7887 | ·1427 | 66·16 | 4·88 | |
| (3.) | ·3733 gram.* | ·9142 | ·1780 | 66·79 | 5·29 | |
| | | | Mean..... | 66·40 | 4·97 | 66·05 : 4·59 |

which agree with the formula $nC_{12}H_{10}O_4$.

When an alcoholic solution of baphiin is mixed with acetate of lead (also in alcoholic solution), a white precipitate is thrown down, insoluble in alcohol. It is washed thoroughly with alcohol, and dried over sulphuric acid. While drying it turns brown, perhaps in consequence of oxidation. It probably consists of plumbic baphate. The alcoholic filtrate from this precipitate, when mixed with water, yields a crystalline precipitate of *baphinitin*. When baphiin is boiled with aqueous potash, the same reaction takes place as with alcoholic plumbic acetate; if the potash-solution be not dilute, other bodies are produced. The potassic baphate, in presence of excess of potash and acid, rapidly colours, so that it requires immediate filtration into hydrochloric acid to prevent further decomposition.

### *Baphic Acid.*

When the alcoholic solutions of acetate of lead and baphiin are mixed, a white precipitate falls, which is probably plumbic baphate. The acid itself is obtained by boiling baphiin with aqueous potash, filtering, and adding hydrochloric acid to the filtrate. It then falls out as a yellowish-white powder, to be purified by placing on the filter (without washing), drying in the air, extracting with anhydrous ether, and evaporating the ethereal solution. Purified still further by repeated crystallisation, it presents itself in the form of white nacreous scales, very readily soluble in alcohol, and especially in ether (even in the cold), insoluble in water. Its ammoniacal solution instantaneously

* New preparation.

precipitates metallic silver from the nitrate. An attempt to prepare a barium salt met with no success. The following analyses were made:—

| | Subs. | Carb. dioxide. | Water. | Carbon. | Hydrogen. | $C_{24}H_{22}O_{10}$. | $C_{24}H_{22}O_9$. |
|---|---|---|---|---|---|---|---|
| (1.) | ·1268 gram. | ·2850 | ·0528 | 61·29 | 4·63 | | |
| (2.) | ·2999 „ | ·6940 | ·1144 | 63·11 | 4·24 | | |
| (3.) | ·2779 „ | ·6520 | ·1059 | 63·99 | 4·23 | | |
| (4.) | ·5385 „ | 1·2208 | ·2444 | 61·80 | 5·04 | | |
| (5.) | ·3105 „ | ·7047 | ·1410 | 61·87 | 5·05 | | |
| (6.) | ·5275 „ | 1·1872 | ·2371 | 61·38 | 4·99 | (61·28 : 4·67) | (63·43 : 4·85) |

*Lead salt.*—Prepared by adding the acid, or an alcoholic solution of baphiin, to an alcoholic solution of plumbic acetate, and washing with alcohol. It is at first white, but dries up to a brown mass over sulphuric acid. The results of the analysis of different preparations are unsatisfactory.

| | Subs. | Carbon dioxide. | Water. | Plumbic oxide. | Carbon. | Hydrogen. | Lead. |
|---|---|---|---|---|---|---|---|
| (1.) | ·6414 gram. | — | — | ·2908 | — | — | 42·09 |
| (2.) | ·5065 „ | — | — | ·2432 | — | — | 44·57 |
| (3.) | ·6992 „ | ·8589 | ·1564 | — | 33·50 | 2·48 | — |

An example of the splitting up of an organic compound into an acid and an indifferent substance like baphinitin is to be found in the case of athamantin (*Ann. Chem. Pharm.*, li, 315), which, on boiling with potash, gives valeric acid and oreoselone—

$$C_{24}H_{30}O_7 = 2C_5H_{10}O_2 + C_{14}H_{10}O_3.$$

*Baphinitin.*

This is the insoluble product, and the chief one, when baphiin is boiled with aqueous potash: it is found in the alcoholic mother-liquid when baphiin and plumbic acetate are brought in contact in alcohol. It is white, having the odour of the original baphiin still more strongly developed; it dissolves with moderate freedom in alcohol and ether, and crystallises in needles. It is insoluble in water. On analysis it gave results leading to the formula $nC_4H_4O$.

| | Subs. | Carb. dioxide. | Water. | Carbon. | Hydrogen. | $nC_4H_4O$. |
|---|---|---|---|---|---|---|
| (1.) | ·3175 | ·8186 | ·1070 | 70·32 | 5·85 | |
| (2.)* | ·2613 | ·6667 | ·1376 | 69·59 | 5·85 | |
| (3.)† | ·3174 | ·8228 | ·1738 | 70·69 | 6·09 | (70·59 : 5·88) |

Treated with strong sulphuric acid, and afterwards with water and carbonate of barium, it yields a solution from which sulphuric acid

* New preparation. † Burned with chromate.

precipitates sulphate of barium, and which yields on evaporation a deliquescent barium salt.

*Baphinitone.*

When baphiin is boiled with strong aqueous potash, air being excluded as much as possible during the operation, there is left undissolved a mixture of three substances;—(1) baphinitin, which dissolves in alcohol and ether with moderate ease; (2) baphinitone, which is very easily soluble in these liquids; and (3) a small quantity of an unexamined body, fusing at 164·1° (corr.), very sparingly soluble in alcohol, even when hot, and separating therefrom in granular crystals. Baphinitone is prepared by treating the part of baphiin which is insoluble in aqueous potash with cold alcohol, which readily dissolves the baphinitone, and but little baphinitin. The solution is evaporated and the treatment repeated, till the crystals thus obtained, after drying over sulphuric acid, fuse at or near 88° C. Baphinitone crystallises from alcohol in hemispherical masses, composed of radiating crystals, beautifully white and lustrous. It is insoluble in water. On analysis it gave the following numbers:—

| | Subs. | Carb. dioxide. | Water. | Carbon. | Hydrogen. | $C_{26}H_{26}O_6$. |
|---|---|---|---|---|---|---|
| (1.) | ·2910 | ·7648 | ·1666 | 71·68 | 6·36 | |
| (2.) | ·1961 | ·5130 | ·1035 | 70·93 | 5·29 | (71·89 : 5·99) |

When an ethereal solution of baphinitone is treated with an ethereal solution of bromine, the latter is decolorised: and on evaporating off the ether, a white substance remains, which, after washing with alcohol or ether (in both of which it is almost insoluble), is pure tribromobaphinitone.

*Tribromobaphinitone* separates from a hot ethereal solution in small granules. As first prepared, it appears to consist of a compact mass of very small, snow-white needles. It fuses, with sudden blackening, at 180·2° (corr.). It yielded on analysis numbers which agree very well with the formula, $C_{26}H_{23}Br_3O_6$.

| Sub. | Carb. dioxide. | Water. | Carbon. | Hydrogen. | $C_{26}H_{23}Br_3O_6$. |
|---|---|---|---|---|---|
| ·5409 | ·9191 | ·1741 | ·46·34 | 3·58 | (46·49 : 3·43) |

Baphiin, baphinitone, and the substance least soluble in alcohol which occurs with the latter, are all coloured orange-yellow by sulphuric acid; with nitric acid an orange-red is obtained, changing to green.

The molecular formulæ of the above bodies are somewhat complex, and there do not appear to be ready means of determining them with precision. Taking, however, that of baphinitone to be precisely deter-

mined, we may fairly assume a $C_{20+n}$ formula for all these bodies. We shall then have the following series:—

| | |
|---|---|
| Baphiin ..... | $C_{24}H_{20}O_8$ |
| Baphic acid ..... | $C_{24}H_{22}O_{10}$ [$O_9$?] |
| Baphinitin ..... | $C_{24}H_{24}O_6$ |
| Baphinitone ..... | $C_{26}H_{26}O_6$ |

*Colouring Matters.*

Barwood contains at least three colouring matters. Ether dissolves out two of these: one (A) which is less soluble, and obstinately adheres to the baphiin, and another more soluble (B), which is easily got rid of. After the extraction with ether is complete, alcohol dissolves a third (C). All are insoluble in benzol; all give purple lakes with plumbic acetate, and purple colorations with alkalis.

(A.) The solubility of this body in ether diminishes after exposure to air. It may be purified from baphiin by boiling with benzol, in which the latter dissolves. It is a bright red powder.

(B.) Crystalline; dissolves easily in boiling alcohol. A strong solution cuts off the blue, and nearly all the green of the spectrum—the blue first. The same solution, mixed with hydrochloric acid, becomes darker, transmits the blue faintly, and very much obscures the green; the yellow and red are transmitted. The solution, after the addition of the acid, on mixing with ammonia or potash, becomes deep pink; the green and blue are much obscured, while the red is left, and the yellow is cut off, and replaced by a black band.

(C.) The green is more absorbed by this colour in alcoholic solution than by (A). When the solution is moderately strong, a black band appears in the yellow. When hydrochloric acid is added, the green is more obscured, and the yellow is still decidedly effaced, notwithstanding the dilution; the blue is nearly removed; the red remains. When ammonia is added to the solution after the action of hydrochloric acid, the colour becomes intensely purple; the red ray is transmitted, the yellow is effaced, the green scarcely visible. C acts on the green and yellow more than A.

N.B.—It has been stated that the "colouring matter" of barwood is identical with santonin. The above renders this very improbable.

# ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

## General and Physical Chemistry.

**On the Observation of the Ultra-red portion of the Spectrum by means of Phosphorescent Substances.** By EDM. BEQUEREL (Compt. rend., lxxxviii, 249—255).

WHEN the ultra-red portion of the spectrum is directed on a phosphorescent substance, such as a sulphide of an alkaline earth, the phosphorescence disappears, but light bands remain, corresponding with dark bands in the red spectrum. These are, however, not distinct. By using two prisms, the author superimposes the violet portion of the spectrum of the one on the red portion of the other; in the ultra-red portion of the spectrum the phosporescent matter, excited by the ultra-violet portion of the second spectrum has its phosphorescence destroyed, but unequally; and a portion corresponding with the ultra-red is bright in certain places and dark in others. All phosphorescent bodies do not show this phenomenon, for the substance must neither remain phosphorescent too long, nor lose its phosphorescence too quickly. The best substance is phosphorescent hexagonal blende. With this substance the author discovered that the active part of the ultra-red extends beyond A rather farther than A is distant from the double line D. The lines observed are:—Beyond A, two bands or lines as strong as A, named by the author $A_1$ and $A_2$; then a group of four bands or lines, grouped as A′ $A'_1$, $A'_2$, $A'_3$; the first three are nearly equidistant from each other, and the fourth farther removed; and a large band A‴, near the limit of vision, nearly as far from A as A is from D; it appears to be identical with that observed by Fizeau and Foucault, in 1847. There appear to be one or two bands beyond A‴, where the spectrum is very intense. A very active portion appears to lie between A″ and A‴. This same activity was shown in the spectrum of the Drummond light.

The wave-length of the bands in this portion of the spectrum was ascertained by interference.

| | Part of the spectrum. | | Index of refraction. | Wave length. |
|---|---|---|---|---|
| Ultra-red | A‴ | Least refracted part | — | 1310 |
| | | Middle..... | — | 1265 (?) |
| | | Most refracted .... | 1·5877 | 1220 |
| | A′ ..... | | 1·5992 | 840 |
| Luminous spectrum | A ..... | | 1·6051 | 761·5 |
| | B ..... | | 1·6114 | 687·3 |
| | D ..... | | 1·6240 | 589·2 |

The band A‴, therefore, lies between 1,200 and 1,300.

W. R.

**Magnesium in the Sun.** By M. TACCHINI (Compt. rend., lxxxii, 1385—1387).

SPECTROSCOPIC observations of the sun, extending over the latter part of May, 1876, showed that at that time—with a marked paucity of protuberances, of hydrogenic clouds, and of eruptions of metallic elements—the circulation of magnesium in the solar atmosphere continued to be very active. It was also observed that, concomitant with this last condition, the granulations and the faculæ were very distinct, while the absence of sodium at this epoch of minimum of spots, seems to indicate that this substance is connected with their formation.

R. R.

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**Electro-motive Order of certain Metals in Potassium Cyanide with reference to the use of this Salt in Milling Gold.** By W. SKEY (Trans. and Proceedings of the New Zealand Institute, 1876, 334—337).

THE author had an opportunity of noticing the marked effect of potassium cyanide in preventing the flouring of mercury used in working off the blanketings. These materials have as a rule an acid reaction, caused by the presence of ferric or ferrous salts in solution, and it is to the former of these salts, that what is commonly known as "flouring" in the process cited above, is mainly due; such salts either oxidising or chlorodising the surface of any mercury they may be in contact with, and thus forming a compound, which, being insoluble in water, prevents amalgamation. Potassium cyanide acts on such mercurial compounds by decomposing them and dissolving their constituent portions, keeping the surface of the mercury metallic. A portion of the mercury used is dissolved, and another, though much smaller portion, may be dissolved from the metal itself by the direct action of the potassium cyanide on it, aided by the free oxygen always present; this happens if no metal is dissolved in the mercury used, having a greater affinity for cyanogen than mercury. It must further be remembered, that both gold and silver are not quite insoluble in cyanide. The loss of metal, which falls upon the mercury, gold, or silver of these blanketings, depends therefore entirely upon the relative affinity of these metals for this salt. Now it is distinctly affirmed that neither gold, silver, or platinum directly precipitates mercury from its solution, but on investigating this subject the author found that in reality mercury is not positive, but very decidedly negative to gold or silver in potassium cyanide, gold and silver being dissolved in mercuric cyanide, while mercury is precipitated.

The following is a list worked out by the author, showing the electromotive order in potassium cyanide of various metals occurring in gold fields, or being employed for milling gold. It runs from negative downwards to positive:—

| | |
|---|---|
| Carbon. | Lead. |
| Platinum. | Gold. |
| Iron. | Silver. |
| Arsenic. | Tin. |
| Antimony. | Copper. |
| Mercury. | Zinc. |

All other ores occurring in nature are mostly negative to the whole series. Thus it is shown, that whenever potassium cyanide is used to assist in the amalgamation of blanketings, the loss falls upon the gold and silver present, the mercury being positively protected from the action of this salt by these more valuable metals.

D. B.

## New Form of Galvanic Battery. By G. LECLANCHÉ (Compt. rend., lxxxiii, 54—56).

THE author describes a modification of the battery devised by him ten years ago. He now dispenses altogether with a porous vessel, and instead of a block of carbon surrounded by a loose mixture of manganese dioxide and broken gas-coke, he now uses as negative element a solid block, composed of an intimate mixture of manganese dioxide (40 parts), gas-coke (55 parts), and shellac (5 parts). This mixture is compressed by hydraulic pressure in steel moulds heated to 100°. The addition to the mixture of 3 or 4 per cent. of acid potassium sulphate reduces resistance, and serves to dissolve the zinc oxychloride which becomes deposited in the pores of the block.

The electromotive force of a cell of the new battery is about 1·5, that of a Daniell's cell being 1.

J. R.

## On the Specific Heat of Gases. By E. WIEDEMANN (Pogg. Ann., clvii, 1—42).

THE author commences this paper by a criticism of the method and apparatus used by Regnault in his investigations on the same subject, and then enters on a full and detailed description of his own apparatus. This portion is so full of detail unsuited for abstraction, that reference to the original paper is recommended for its consideration. The gases examined were atmospheric air, hydrogen, carbon monoxide, carbon dioxide, ethylene, nitrous oxide and ammonia.

*Atmospheric Air.*—Perfectly dry and pure air having been taken for the experiments, the mean of the numbers obtained was 0·2389, the greatest deviation from this being 0·0025. These numbers agree closely with those obtained by Regnault, the numbers found by him extending between 0·23536 and 0·23890, whilst those of the author extend between 0·2374 and 0·2414, the mean found by the author, 0·2389, not differing one per cent. from that obtained by Regnault, 0·23751.

*Hydrogen.*—Prepared from zinc and sulphuric acid, and purified in the usual manner, gave, as the mean of the results, 3·410, the greatest variation from this being 0·004. For the specific heat in reference to volume, by multiplying the specific weight 0·0692 by the number obtained, 3·410, the value 0·2358 was obtained.

*Carbon Dioxide.*—The result of the experiments between 100° and 25° gave, as mean, the number 0·2088, the greatest variation being 0·0027. The results between 150° and 25° gave as mean 0·2152, the greatest variation being 0·0019, and between 200° and 25°, 0·2917, with a variation of 0·0033. The numbers obtained by the author

appear as good as those obtained by Regnault, his numbers for 210° and 10° varying between 0·21416 and 0·21844, those for the specific heat between 100° and 10° between 0·20086 and 0·20308. The following arrangement shows a comparison of the true specific heats at the different temperatures calculated from the author's numbers given above with those obtained by Regnault:

| | | Wiedemann. | Regnault. |
|---|---|---|---|
| For— | 0° | 0·1952 | 0·1870 |
| | 100° | 0·2169 | 0·2145 |
| | 200° | 0·2387 | 0·2397 |

*Carbon Monoxide.*—The gas in this case was prepared from potassium ferrocyanide and most carefully purified. The determinations between 100° and 25° gave as mean 0·2425, with greatest deviation 0·0026, this determination agreeing closely with Regnault's, viz., 0·2450.

*Ethylene.*—Between 100° and 25° the mean of the results was 0·3880, the greatest deviation being 0·0093. Between 200° and 27° the mean was 0·4290, with a deviation of 0·0108; this last result does not differ much from 0·404, the number obtained by Regnault at the same temperature. Ethylene, like $CO_2$ and $N_2O$, shows great change of specific heat with the temperature, the true specific heats for the different temperatures being 0°, 0·3364; 100°, 0·4189; 200°, 0·5015.

*Nitrous Oxide.*—Between 100° and 25° the number obtained, 0·2126, between 200° and 25°, 0·2241; from these measurements the calculated specific heats at different temperatures were as follows: 0°, 0·3014; 100°, 0·3362, and 200°, 0·3172.

*Ammonia.*—In the case of this gas 12 experiments were made, giving, as mean between 100° and 25°, the result 0·5202, the greatest deviation from this being 0·0118. Eleven experiments made between 200° and 25° gave as the mean result 0·5356, with the greatest deviation 0·0137.

A comparison of the author's results with those obtained by Regnault, show that the method used by the former is not inferior to that of Regnault in accuracy; and as the quantity of water in the author's calorimeter is only $\frac{1}{10}$ the quantity used by Regnault, so, $\frac{1}{10}$ the quantity of gas is sufficient to obtain an equal rise in temperature. By this important economy of material it is thus possible to give the experiments greater range in a comparatively shorter time. In the following table is given a comparative view of the resulting numbers:—

Specific heats of equal weights.

| | I. | II. | III. | IV. |
|---|---|---|---|---|
| | 0°. | 100°. | 200°. | |
| Air | 0·2389 | — | — | 0 |
| Hydrogen | 3·410 | — | — | 0 |
| Carbon monoxide | 0·2426 | — | — | 0 |
| Carbon dioxide | 0·1952 | 0·2169 | 0·2387 | 22·28 |
| Ethylene | 0·3364 | 0·4189 | 0·5015 | 49·08 |
| Nitrous oxide | 0·1983 | 0·2212 | 0·2442 | 23·15 |
| Ammonia | 0·5009 | 0·5317 | 0·5629 | 12·38 |

| | Specific heats of equal volumes. | | | | |
|---|---|---|---|---|---|
| | V. | VI. | VII. | VIII. | IX. |
| | 0°. | 100°. | 200°. | Specific weight. | $\frac{PV}{P'V'}$ |
| Air | 0·2389 | — | — | 1 | 1·00215 |
| Hydrogen | 0·2359 | — | — | 0·0692 | — |
| Carbon monoxide | 0·2346 | — | — | 0·967 | 1·00293 |
| Carbon dioxide | 0·2985 | 0·3316 | 0·3650 | 1·529 | 1·00722 |
| Ethylene | 0·3254 | 0·4052 | 0·4851 | 0·9677 | — |
| Nitrous oxide | 0·3014 | 0·3362 | 0·3712 | 1·5241 | 1·00651 |
| Ammonia | 0·2952 | 0·3134 | 0·3318 | 0·5894 | 1·01881 |

The 1st, 2nd and 3rd columns contain the true specific heat of the gas at 0°, 100° and 200° in reference to the unit of weight. The 4th gives the difference of the true specific heat at 0° and 200°, expressed in percentage of the specific heat at 0°. The 5th, 6th and 7th columns contain the true specific heat in reference to the unit of volume, the specific heat of the unit volume of air being taken as equal to 0·2389. The 8th column contains the specific weights of the respective gases, whilst the 9th gives the proportion made by Regnault of the products of the volumes V and V′, and the pressures P and P′ when P is at a pressure of one, and P′ at a pressure of two atmospheres. The product of these being identical in the case of perfect gases, this deviation from unity, where it occurs, may serve as a measure of the deviation of such gases from the perfect gaseous condition.

The specific heat determined in the above experiments appears to be composed of two parts, first of the frictional heat (heat caused by work) expended on the expansion of the gases in overcoming outside pressure, which can be reckoned from the coefficient of expansion and heat-equivalent to be 0·06902 units of heat in changing the temperature of 1 gram of air one degree; secondly, the heat employed in the internal work of the gas itself, which also may be measured directly from the knowledge of the specific heat in the constant volume D. The author thinks that the determination of the separate parts of the heat of molecular motion of which the specific heat is composed in constant volumes, of the heat of atoms according to Naumann, and also the attempt to establish simple relationships between the two, is still premature, inasmuch as the unequal alteration of the specific heat and the temperature would make these have different relations between different temperatures. The alteration of the specific heat of gases with the temperature cannot be explained by the deviation of these gases from a perfect gaseous state. For instance, ammonia, although more remote from the perfect gaseous state than nitrous oxide or carbon dioxide, has still smaller variations with the temperature than these latter. That the difference in the coefficients of expansion cannot influence these variations may be seen from the minute differences of the same for different gases. To deduce the cause of the marked differences of the sp. heat of one of the bodies composing the gas in question, as carbon or nitrogen, is not possible, for, as in the case of

air, the specific heat of nitrogen does not alter with the temperature, as also happens in the case of the carbon in all carbon compounds, and likewise that in carbon monoxide. If this were not so, it would be necessary to suppose, like Weber (*Pogg. Ann.*, 1875, Bd. 154, p. 578), that the carbon possessed different properties from those exhibited when it existed in combination in carbon dioxide. Perhaps the variation in the specific heat with the temperature may be explained by this fact, that, on warming the gas, there arises a gradual dissociation which eventually causes a looseness in the attraction of the different atoms, and produces a waste of heat. The heat arising in the decomposition of nitrous oxide need not contradict this explanation; H. Favre accounts for this development of heat by the supposition that it is produced by the change of the oxygen from an active into an inactive condition. With the low temperatures used in the author's experiments, the dissociation most probably has not been advanced to the state of perfect decomposition, and this change therefore would not have taken place.

J. M. T.

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## On the Expansion and Specific Heat of Fusible Alloys.

By W. Spring (Ann. Chim. Phys. [5], vii, 178—228).

The first part of this memoir is devoted to a historical account of the development of the subject of specific heat from the time of Wilcke and Black to the present day. The author then describes the method adopted by himself to measure the volumes of the four following fusible alloys at temperatures between 0° and 120°:—

I. An alloy of bismuth, tin, and lead, known as Rose's alloy, and having the composition represented by the formula $Bi_7Sn_6Pb_4$.

II. Darcet's alloy of bismuth, tin, and lead, in the proportions represented by the formula $Bi_{13}Sn_{10}Pb_8$.

III. Wood's alloy, the composition of which is represented by the formula $Bi_4PbCd_2Sn_2$.

IV. Lipowitz's alloy, represented by the formula $Bi_{11}Pb_6Sn_5Cd_4$.

The volumes of these alloys at different temperatures were determined by means of an apparatus resembling in principle a large thermometer. For details of the construction and use of this apparatus, the original memoir must be referred to. Briefly, the method consisted in comparing the expansions produced by heating in a bath a glass vessel filled, first with pure olive oil, and then partly with an alloy and partly with olive oil, the temperature of the oil being indicated by a thermometer, the bulb of which occupied the centre of the glass vessel. The volumes thus determined showed great irregularities in the expansion of the alloys. The alloy No. I expanded from 0° to about 40°, and contracted from that point to about 55°, at which temperature it occupied a less volume than at 0°. From 55° it expanded again up to its melting point at 90°, where it underwent a sudden expansion, and afterwards continued to expand slowly up to 120°. Alloy No. II expanded from 0° to 33°, contracted from 33° to 43°, and afterwards expanded continuously up to 120°, with a sudden great expansion at its melting point—about 90°. Alloy No. III con-

tracted slowly from 0° to about 25°, then expanded continuously up to 120°, with a sudden great expansion at 80°, when it melted. Alloy No. IV expanded slowly from 0° to about 25°, contracted from 25° to 45°, where its volume was less than at 0°, and then expanded continuously up to 120°, melting at about 70°.

The specific heats of the alloys at different temperatures were determined by a modification of the method of cooling, which was found by test-experiments with graphite and mercury to give results almost identical with those obtained by Regnault and by Dulong and Petit by other methods.

Some of the results arrived at are given in the following table:—

| Alloy. | Temperature. | Volume. Volume at 0° = 1. | Specific Heat. |
|---|---|---|---|
| I. | 29·0° | 1·00682 | 0·0474 |
| | 38·5 | 1·01295 | 0·0562 |
| | 68·2 | 1·00700 | 0·0545 |
| | 100·0 | 1·04500 | 0·0881 |
| II. | 29·0 | 1·01485 | 0·0621 |
| | 41·5 | 1·01600 | 0·0528 |
| | 56·5 | 1·02493 | 0·0650 |
| | 101·3 | 1·09980 | 0·8901 |
| III. | 53·25 | 1·00265 | 0·0575 |
| | 93·00 | 1·03735 | 0·0918 |
| IV. | 28·0 | 1·0321 | 0·0634 |
| | 50·0 | 1·00115 | 0·0544 |
| | 90·5 | 1·05042 | 0·0625 |

An inspection of this table shows that the variations in specific heat follow those of volume, independently of the temperature. For instance, the volume of the alloy I at 38° is greater than at 29°, and its specific heat is also greater; whilst at 68° the volume and the specific heat are both less than at 38°. In general, when a body is heated it expands, and its specific heat becomes greater; and it is usual to regard the rise of temperature as the cause of the increased specific heat, without attaching much importance to the phenomena of expansion. But, seeing that, in cases where the volume contracts with rise of temperature, the specific heat at the same time becomes less, would it not be more correct (the author asks) to regard the specific heat as a function of the volume rather than of the temperature, if indeed it is at all influenced by the latter? It is admitted that the molecules of a body are subject to a force which tends to bring them together, and that the action of heat has the opposite effect. If it be further granted that the molecular force is a function of the distance of two molecules, then the quantity of work to be done in order to increase that distance by a given amount will be greater the greater the distance of the molecules asunder (*i.e.*, the greater the volume); and consequently the specific heat should be a function of the volume.

J. R.

**New Method for Accurately Determining the Melting Points of Metals, and also of Bad Conductors of Heat.** By C. HIMLY (Dingl. polyt. J., ccxx, 529—534).

As the difficulties of accurately determining the melting points of bad conductors of heat, *e.g.*, of fats, &c., especially if they at the same time possess a considerable latent heat, and the imperfect method of placing the substance under investigation in a tube and observing the melting of the former by a thermometer put by the side of the tube, are generally known, the author applied an improved method, by which he could determine the melting of both good and bad conductors of heat and electricity.

The thermometers employed for this method have thin ogivally-sealed mercury receivers, similar to retort thermometers, which are silvered over chemically with a liquid made by dissolving 17 parts of silver nitrate and 28 parts of sodio-potassic tartrate, each in distilled water, and mixing the solutions.

The precipitate formed is allowed to settle, the liquid decanted and replaced by two or three washings with distilled water. The silver tartrate is then put into a closed vessel after being mixed with a small quantity of distilled water. When required for use a portion of the mixture is placed in a glass vessel, and very dilute ammonia added. Successful results can be obtained only by avoiding all excess of ammonia; a small quantity of the salt will in this case remain undissolved. After dilution with distilled water the silvering will at once commence. The thermometers are quickly plunged into the solution. As the coating is but very thin, it is best to strengthen it by placing the silvered receivers in the usual copper-vitriol solution through which a weak electric current is passed. Before doing this a thin copper wire, twice the length of the thermometer-tube, is attached to the receiver, passed up the tube, and fixed at the top with an india-rubber ring. For good conductors the copper coating may be rather strong.

To determine the melting point of metals and conductors of electricity a U-tube is employed, the sides of which are 10 cm. long, and somewhat wider than the thermometer used. The metal is cast into small rods of the width of the thermometer and placed in the one side of the tube and the thermometer in the other. Both should be fixed very near to the bend of the tube without touching one another. A wire is also attached along and down to the bend of the tube containing the rod of metal, which can be connected with a galvanic element. The U-tube is put into an iron vessel filled with either mercury or Rose's metal mixtures. Between the conducting wires of the thermometer and the metal an electric bell is introduced, so that the whole circuit is interrupted merely in the bend of the tube. As soon as a temperature has been reached at which the rod of metal melts, the fluid metal will complete the electric circuit, while at the same time the bell rings and the reading of the thermometer can take place. For very high temperatures a pyrometer may be used.

For non-conductors of heat and electricity the same thermometer with its wire may be used. The substances to be determined are

melted and the mercury receiver of the thermometer dipped into the melted mass as soon as it shows signs of solidifying. A coating of 1—2 mm. thickness suffices. An iron-bath is further required in which through a hole in the lid a thin porcelain crucible filled with mercury is immersed as far down as possible. The liquid used for warming the bath consists of glycerin, or of a solution of calcium chloride in glycerin. For temperatures above 200° the mercury-bath would have to be employed. The thermometer with its coating of the non-conductor is fixed into the middle of the porcelain crucible filled with mercury and the wire connected with the bell. The other wire is passed along the side into the mercury-bath. The glycerin vessel is then heated slowly, and since the surface of the non-conductor is the same as that of the thermometer, the latter must, at the moment of the melting at which the bell rings, indicate the true melting point with great accuracy.

Finally the author points out that the metal in the tube must be immersed below the surface of the metal-bath, and heated regularly on all sides. It is further necessary that the bend of the tube be not too sharp or irregular, so as not to interfere with the flowing of the fluid metal.

D. B.

**Determination of the Melting Points of Butter and other Fats.** By T. REDWOOD (Pharm. J. Trans. [3], vi, 1009).

MERCURY is poured into a small beaker to the depth of about an inch; this small beaker is then supported inside another one four and a half inches deep by three inches in diameter, and cold water is poured into the outer beaker, so that its surface shall be half an inch above the level of the mercury. These are placed in an iron enamelled basin. A small drop of the molten fat is then put on the surface of the mercury; the fat should be near its setting point, so as not to run over the surface of the mercury. Heat is communicated to the small beaker by pouring hot water into the iron dish. When the temperature is near the melting point, the bulb of the thermometer is brought up to the fat, so that at the moment of fusion the molten fat runs down into the channel formed by the repulsion of the mercury and the thermometer tube.

E. W. P.

**Heat of Formation of Ozone.** By M. BERTHELOT (Compt. rend., lxxxii, 1281—1283).

THE author has determined the heat evolved by the oxidation of arsenious acid in dilute solution by ozone, which he finds to amount to 34·400 heat-units (kil.-degrees) for 8 grams of oxygen absorbed (= 24 grams of ozone destroyed). But the heat evolved in the oxidation of arsenious acid by 8 grams of free oxygen was found by Favre and Thomsen, by indirect methods, to be 19·600 units. This deducted from 34·400 leaves 14·800 units as the amount of heat liberated by the

conversion of ozone into oxygen, or absorbed by the conversion of oxygen into ozone. Putting O = 16,

$$3O = (O_3) \ldots\ldots\ldots\ldots \quad -29{\cdot}600 \text{ heat-units.}$$

Thus the formation of ozone is attended by the absorption of heat, and this heat is liberated in oxidations effected by ozone,—a circumstance which accounts for its great activity.

J. R.

## Inorganic Chemistry.

**Formation and Decomposition of Binary Compounds by the Dark Discharge.** By M. BERTHELOT (Bull. Soc. Chim. [2], xxvi, 101—104).

WHEN a mixture of hydrogen and nitrogen is submitted to the dark discharge, they begin to combine until 3 per cent. by vol. of ammonia is formed; on the other hand ammonia is decomposed by this agent, until the same limit is reached, *i.e.*, until the residual gas contains 9·06 of the original volume.

*Nitrous oxide* is also resolved into its elements; after a few hours the greater part of the gas is decomposed, and a large portion of the nascent oxygen is absorbed by the mercury.

*Nitric oxide* yields nitrogen and a considerable quantity of nitrous oxide, which is then decomposed as above, the free oxygen combining with an excess of nitric oxide to peroxide, which attacks the mercury.

*Hydrogen sulphide* is resolved into hydrogen, sulphur, and hydrogen persulphide, according to the equation—

$$8H_2S = 7H_2 + H_2S_x + (8 - x)\,S.$$

*Hydrogen selenide* yields analogous products.

*Hydrogen phosphide* is decomposed according to the equation—

$$4PH_3 = 5H_2 + P_4H_2.$$

Chlorine, bromine, and the fluorides of boron and silicon are not changed.

*Sulphur Dioxide.*—One-tenth was resolved into oxygen, and sulphur insoluble in carbon sulphide.

*Cyanogen* is rapidly transformed into paracyanogen.

*Carbon monoxide* yields carbon dioxide, and Brodie's oxide, $C_4O_3$—

$$5CO = CO_2 + C_4O_3.$$

This oxide is a brown, amorphous body, which is soluble in water and absolute alcohol, but not in ether. It has an acid reaction, and gives with silver nitrate, lead acetate and baryta-water, brown, amorphous precipitates. On heating it to 300—400° in an atmosphere of

nitrogen, it yields equal volumes of carbon monoxide and dioxide, and a new dark brown oxide, $C_8O_3$—

$$3C_4O_3 = 2CO + 2CO_2 + C_8O_3.$$

When this oxide is more strongly heated, it is decomposed, carbon still containing oxygen being left behind.

*Methane*, *ethane*, and *ethene* yield a little acetylene, free hydrogen, and resinous condensation-products. Marsh-gas produces also a very small quantity of a liquid smelling like turpentine, while ethane yields some ethene, and the latter forms also the liquid, $C_{10}H_{16\cdot6}$, discovered by Thénard.

The dark discharge tends, like the spark, to resolve compounds into their elements, but at the same time to recombine the latter, and thus a state of equilibrium sets in. In the case of the dark discharge, a portion of the free elements combines with the compound to form products of condensation, which, on account of their fixity, are not further changed by the discharge. Under the influence of the spark such products are generally not formed, probably on account of the high temperature.

C. S.

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## Researches on Silicon, its Subfluorides, Subchlorides, and Oxychlorides, and the Organic Derivatives of the Latter.

By L. Troost and P. Hautefeuille (Ann. Chim. Phys. [5], vii, 453—476).

When silicon is fused in a current of hydrogen, and one bubble of silicon fluoride is allowed to enter the tube, thick fumes are formed as this gas comes into contact with the silicon, and afterwards a fine brown powder is deposited, consisting of amorphous silicon. On admitting more fluoride, this process goes on until the whole of the fused silicon is converted into the amorphous modification. If, however, the fluoride is admitted very slowly, a ring of crystallised silicon is formed at that part of the porcelain tube which is just below red heat, and on continuing this operation for an hour, the crystals increase, leaving only a small aperture in the centre.

This apparent volatilisation of silicon in a current of its fluoride also takes place by producing the voltaic arc between two pieces of silicon in an atmosphere of its fluoride. A smoky flame appears, having a brilliant envelope containing finely divided silicon, which is gradually deposited on the inner surface of the vessel. When the distance between the poles is as large as possible, the light shows a most brilliant violet colour. If in place of a powerful battery an induction coil is used, amorphous silicon is also formed, but only slowly.

Silicon chloride acts like the fluoride, and even more rapidly; thus in one hour five grams of silicon were volatilised. The deposit is either amorphous or crystalline, the crystals being formed in the part of the tube having the temperature 500—800°; they are well defined, and show a compact fracture.

The authors have previously shown that this apparent volatilisation

of silicon is due to formation of lower fluorides or chlorides, which are stable at a low temperature and at red heat, but undergo dissociation at intermediate temperatures. The hydrides of selenium and tellurium have the same remarkable property, for Ditte has shown that they are resolved at a certain temperature into their elements, which unite again when more strongly heated.*

*Silicon sesquichloride*, $Si_2Cl_6$, is most conveniently obtained by using Deville's hot and cold tube. Through the axis of the latter a smaller tube passes, which opens in the middle of the annular space, and through which the vapour of the tetrachloride is led to the fused silicon. The apparatus is provided with a worm-condenser, from which the condensed vapours are carried back to the vessel containing the tetrachloride.

The product contains, besides the sesquichloride, an excess of tetrachloride and some oxychloride, due to the presence of oxygen which is difficult to exclude completely.

Silicon sesquichloride is a very mobile liquid, having at 0° the specific gravity, 1·58, and solidifying at − 14° to plates resembling boric acid. It boils at 146—148°, and its vapour density at 239·4° is 9·7. When its vapour is strongly heated in presence of air, it takes fire; but on heating it in a closed vessel, it begins slowly to decompose at 350°, while at 800° it is almost completely resolved into silicon and the tetrachloride. But on heating it rapidly to above 1000°, the tension of dissociation diminishes with the increase of temperature, and disappears gradually.

Cold dilute ammonia decomposes the sesquichloride, with formation of free hydrogen and silicic acid, and with water at 0° it yields the hydrated sesquioxide. This body reduces potassium permanganate rapidly in the cold, but chromic acid is very slowly reduced by it. At the common temperature it does not act on gold chloride, or on a solution of selenious acid. It does not retain hydrochloric or sulphuric acid, which are completely removed by washing, but when immersed in nitric acid, it takes up a certain quantity, which cannot be removed by washing, and is given off at a temperature only a little below that at which the sesquioxide is oxidised to silica.

*Silicon protochloride* is formed, besides the sesquichloride, when a very high temperature is employed. It cannot be separated from the oxychlorides present; its vapour takes fire in the air, at a temperature below red heat, and is decomposed by dilute ammonia, yielding a larger proportion of hydrogen than the sesquichloride. With water at 0°, it yields a protoxide, which reduces potassium permanganate, chromic acid, gold chloride, and selenious acid, and seems to have basic properties.

*Silicon subfluoride* is formed when a rapid current of the tetrafluoride is passed over silicon, heated to near the temperature where porcelain softens. At a red heat it is resolved into silicon and the tetrafluoride, and to obtain it the vapours must therefore be rapidly cooled. It is a

* *Note by the Abstractor.*—Another example is furnished by nitrogen trioxide, which, as Hassenbach has found, is formed when a mixture of nitrogen peroxide and nitric oxide is passed through a hot tube; the liquid thus obtained is stable only below − 2°; above this temperature, it is resolved into the above two oxides.

light, white, volatile powder, which acts on the different reagents like the sesquichloride, and yields the same hydrated oxide, and appears therefore to be $Si_2F_6$.

*Oxychlorides of Silicon.*—These compounds are formed by the action of a bright red heat, or the electric spark, on a mixture of the tetrachloride and oxygen, but are best prepared by repeatedly passing a mixture of oxygen and the oxychloride, $Si_2OCl_6$ through a red-hot porcelain tube filled with pieces of porcelain.

The different bodies formed are separated by fractional distillation. The most volatile portions consist of a liquid boiling at 152—154°, and to which the authors, who use the old equivalent weights, assign the molecular formula, $Si_4O_3Cl_5$; probably this compound is a mixture of the oxychlorides, $SiOCl_6$ and $Si_4O_4Cl_8$. The latter is a liquid boiling at 198—202°; its vapour-density at 440° was found to be 15·5.

$Si_8O_{10}Cl_{12}$ is also a liquid, which boils at about 300°, and has the vapour-density 31·2. A fourth oxychloride boils above 400°, and its formula is a multiple of $Si_2O_3Cl_2$; and the last compound is a solid, which does not melt at 440°, and has the empirical formula, $Si_4O_7Cl_2$.

These oxychlorides are also obtained when the compound, $Si_2OCl_6$, is passed alone through a red-hot tube, silicon tetrachloride being formed at the same time, and their formation is quite analogous to that of Berthelot's synthesis of higher hydrocarbons from acetylene.

When to the oxychloride, $Si_4O_4Cl_8$, which is heated to near its boiling point, absolute alcohol is added drop by drop, the ether $(C_2H_5O_6)Si_4O_4$ is formed. It is a mobile liquid, boiling at 270—290°, and having the spec. grav., 1·071 at 0°, and 1·054 at 14·7°; its vapour-density is 19·54. It is soluble in ether and alcohol, but not in water, which decomposes it into alcohol and silicic acid. When ammonia is passed into its ethereal solution the compound $(C_2H_5O)_7NH_2Si_4O_4$ is formed, which is an oily liquid. By continuing the action of ammonia another body, probably $(C_2H_5O)_6(NH_2)_2Si_4O_4$ was obtained. By the action of alcohol on $Si_2OCl_6$, Friedel and Ladenburg obtained the ether $(C_2H_5O)_6Si_2O$, and this yields with ammonia the compound, $(C_2H_5O)_5NH_2Si_2O$, an oily liquid, boiling in a vacuum at about 280°, and which is not readily attacked by water. By the further action of ammonia, the body, $(C_2H_5O)_4(NH_2)_2Si_2O$, is formed, which is very unstable, and could not be obtained pure

The other oxychlorides yield also high-boiling ethyl-compounds.

C. S.

**Some Reactions of the Chlorides of Boron and Silicon.** By L. Troost and P. Hautefeuille (Ann. Chim. Phys. [5], vii, 476—479).

When the vapour of boron chloride is passed through a red-hot porcelain tube, which is not glazed on the inside and contains pieces of unglazed porcelain, the chlorides of aluminium and silicon and aluminium borate are formed. But on using glazed porcelain there is formed, besides the two chlorides, a double chloride of potassium and aluminium, but the glaze is much less attacked than the paste.

On heating pure alumina in a platinum tube, and passing boron

chloride over it, aluminium chloride and borate were produced, while, on treating silica in the same way, the products consisted of silicon chloride and boron trioxide. The oxides of zirconium and titanium behave in the same manner.

Silicon chloride does not attack porcelain or its glaze even at a temperature at which it softens, but pure alumina is attacked by it and converted into the chloride, while zirconium oxide yields zirconium silicate and chloride, and titanium oxide is not changed. From this it would appear that silicon chloride attacks only such oxides as form silicates.

Boron fluoride acts rapidly on red-hot porcelain, with formation of silicon fluoride, and the latter attacks porcelain but slowly, but alumina and zirconia very readily.

While the silicates of aluminium and zirconium which are obtained by means of the chloride are amorphous, those formed by the action of the fluoride are crystalline. The reason of this is, as Deville has shown, that the fluorides of aluminium and zirconium decompose silica and reproduce silicon fluoride, thus giving rise to an apparent volatilisation, by which crystalline silicates are deposited.

C. S.

## Action of different Solutions on Metals. By A. WAGNER (Dingl. polyt. J., ccxxi., 259—263).

WAGNER has tried the effect of different solutions on iron, copper, zinc, lead, tin, and the alloys Britannia-metal, brass, and German silver. The copper was pure, the zinc the ordinary sheet-metal, with 0·68 per cent. of lead, the lead, ordinary sheet. The tin was the pure fused and hammered metal. The Britannia-metal consisted of 90 per cent. tin, and 10 per cent antimony, the brass of 64·5 per cent. copper to 29·8 per cent. zinc and nickel. Strips of the metals and alloys, of equal sizes and thicknesses, were immersed in equal volumes of the solution (11·831 square centimeters area to 100 c.c. of solution). During one week, air free from carbonic acid was passed through the solution; in the second set of experiments, both air and carbonic acid were transmitted. The solutions were of the following degrees of concentration. In 100 c.c. of water were dissolved 0·5 grm. potassium or sodium chloride, 1 grm. of ammonium chloride, 0·83 grm. of magnesium chloride, 1 grm. of potassium sulphate, 1 grm. of nitre, 1 grm. of sodium carbonate, 0·923 grm. of sodium hydrate.

In the table, under I, are the amounts of diminution in weight of the strips of metal, when air was transmitted; II contains those when air and carbonic acid were transmitted. + indicates that the filtered solution contains some dissolved metal if only doubtful traces (?); and if none dissolved, 0.

| Solution. | | Copper. | Zinc. | Lead. | Tin. | Britannia metal. | Brass. | New silver. | Iron. |
|---|---|---|---|---|---|---|---|---|---|
| Distilled water.. | | ? | ? | ? | 0 | 0 | 0 | 0 | 0 |
| | I .. | 1 | 14 | 3 | — | — | — | — | 29 |
| | | + | + | + | 0 | 0 | + | + | + |
| | II.. | 3 | 19 | 8 | — | — | 4 | 4 | 54 |
| Potassium and sodium chlorides | | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | I .. | 4 | 7 | 21 | 6 | 9 | 2 | 1 | 42 |
| | | + | + | + | 0 | ? | + | + | + |
| | II.. | 115 | 38 | 12 | — | 1 | 80 | 61 | 72 |
| Ammonium chloride ..... | | + | + | + | 0 | 0 | + | + | 0 |
| | I .. | 904 | 51 | 12 | 5 | 3 | 269 | 86 | 45 |
| | | + | + | + | 0 | 0 | + | + | + |
| | II.. | 138 | 36 | 5 | — | — | 167 | 116 | 76 |
| Magnesium chloride ..... | | 0 | + | ? | 0 | 0 | + | + | ? |
| | I .. | 5 | 18 | 20 | 1 | 1 | 4 | 3 | 49 |
| | | + | + | + | 0 | ? | + | + | + |
| | II.. | 112 | 54 | 35 | — | 1 | 92 | 67 | 65 |
| Potassium sulphate..... | | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| | I .. | — | 30 | — | 2 | 1 | — | — | |
| | | + | + | 0 | 0 | 0 | + | + | |
| | II.. | 4 | 53 | — | — | — | 4 | 4 | |
| Potassium nitrate | | 0 | 0 | 0 | 0 | 0 | 0 | 0 | |
| | I .. | — | 9 | 14 | 3 | 1 | — | — | |
| | | + | + | + | + | + | + | + | |
| | II.. | 3 | 37 | 20 | 1 | 1 | 3 | 4 | |
| Sodium carbonate.... | | 0 | 0 | 0 | + | + | 0 | 0 | 0 |
| | I | — | 13 | — | 7 | 6 | — | — | — |
| Sodium hydrate .... | | 0 | + | + | + | + | ? | ? | |
| | I | — | 60 | 430 | 220 | 94 | 2 | 1 | |
| Lime water ..... | | 0 | ? | + | 0 | 0 | ? | 0 | 0 |
| | I | — | 3 | 137 | — | — | 2 | — | — |

The above numbers represent milligrams of the respective metals acted upon by the different solutions. The following conclusions drawn from the above table with respect to lead, will exemplify the use of the table.

It will be observed that the effect of distilled water, free from carbonic acid but in presence of air, is to produce a precipitate, but no appreciable solution of the lead. In presence both of air and carbonic acid, however, an appreciable amount of lead is dissolved, the solvent effect being increased threefold by the carbonic acid. Solutions of alkaline chlorides in presence of air free from carbonic acid, produce a considerable precipitate, but no perceptible solution. With carbonic acid, however, though the action was only half as great, yet

much lead was dissolved. A potassium sulphate solution had no effect. A nitre solution, with air free from carbonic acid, had less influence than the chloride solution, no lead being dissolved. With carbonic acid the action was stronger, and some lead was dissolved. Dilute sodium carbonate solution has no effect on lead; sodium hydrate acts strongly, producing no precipitate but much solution. Lime-water produces a reddish-yellow precipitate and considerable solution.

W. S.

**Solubility of the Alkalis in Ether.** By W. SKEY (Trans. & Proc. of the New Zealand Institute, 1876, 338).

IT was found that hydrous ether, when agitated with an aqueous solution of caustic potash or sodium carbonate, then decanted off into clean test-tubes and evaporated in platinum vessels, gave a residue having an alkaline reaction, which was persistent when the residue was gently ignited and dissolved in water, clearly showing that a fixed alkali was present in both cases in the free state, or at least as carbonate. The same results were obtained with lime and magnesia. Sodium bicarbonate, however, dissolves only in minute quantities.

In regard to the solvent power of ether itself, *i.e.*, the anhydrous substance, it was found that dry potassium hydrate mixed with it, gave a marked alkaline reaction, which was more intense than could have been occasioned by any minute trace of alkaline acetate possibly present in the ether.

In special cases, therefore, for isolating and obtaining pure alkaloïds by Stas's process, the use of sodium bicarbonate, or, still better, an earthy carbonate, would be more advantageous than that of caustic alkali.

D. B.

**Decomposition of Moist or Dry Bicarbonates of the Alkalis, by Heat and Reduced Pressure.** By ARM. GAUTIER (Compt. rend., lxxxiii, 275).

THESE bicarbonates were prepared by passing carbonic anhydride over the moist salts, and drying them finally in a current of that gas. Dry sodium bicarbonate is not decomposed in a vacuum by a temperature of 25°, but when heated to 100° in air, it loses nearly all its carbonic anhydride; the last traces require the temperature to be 115° before they are thoroughly expelled. If water be present, it decomposes much more quickly, and the more easily the more water is present. The author objects, on this account, to Matthieu and Urbain's assertion that he is wrong in stating that sodium bicarbonate in the blood decomposes at 100°. Potassium bicarbonate decomposes sensibly in a vacuum between 25—30°. It does not decompose so easily at 100° as sodium bicarbonate, but rapidly in presence of water.

W. R.

**Dissociation of Sodium Bicarbonate at 100°.** By V. URBAIN (Compt. rend., lxxxiii, 543—545).

THIS is a refutation of Gautier's assertion, in a recent number of the *Comptes rendus* (see last abstract), that the sodium bicarbonate of the blood dissociates at 100—115°. It is quite true that ordinary sodium bicarbonate does dissociate; but when it is covered with a layer of albumin, as in blood, this is not the case.

W. R.

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**Pyrophosphates of Lithium, Lithium-sodium, and Lithium-potassium.** By M. NAHNSEN and E. CUNO. (Liebig's Annalen, clxxxii, 165).

BERZELIUS has described a double phosphate of lithium and sodium obtained by evaporating to dryness a mixture of alkaline salts containing lithium with phosphoric acid and a little sodium carbonate, or a mixture of sodium phosphate and a lithium salt. Thinking that this body is really a pyrophosphate, the authors have investigated the nature of the crystalline, very sparingly soluble double salts produced by heating together solutions of sodium pyrophosphate and lithium chloride in varying proportions.

When 1 molecule of the latter and 2 of the former are employed, the crystals have the composition $Li_8Na_{12}P_{10}O_{25}$, or $4Li_2O.6Na_2O.5P_2O_5$, and contain 2—2·15 per cent. of water.

With equal molecular weights of each salt, the composition is $Li_2Na_2P_2O_7$, or $Li_2O.Na_2O.P_2O_5$, the percentage of water being 1·78—2·61.

With 2 molecules of lithium chloride to 1 of sodium pyrophosphate, the crystals had the composition $Li_3NaP_2O_7$, or $3Li_2O.Na_2O.2P_2O_5$, with 10·8—24·75 per cent. of water.

With 5 molecules lithium chloride to 1 of pyrophosphate, the composition was $Li_{10}Na_2P_6O_{21}$, or $5Li_2O.Na_2O.3P_2O_5$, with 12·86—42·3 per cent. of water.

The greater the quantity of water contained in the pressed crystals, the more rapidly did they effloresce in the air. The richer they were in lithium the more distinctly was the lithium crimson flame given, predominating over the sodium yellow. Before the blowpipe, they melted to a transparent bead, becoming white and opaque on cooling.

The analysis of these salts was performed by dissolving them in nitric acid, adding silver nitrate and freshly precipitated hydrate, dissolving the filtrate in nitric acid, removing silver with hydrochloric acid, and finally converting the pyrophosphoric acid in the filtrate into ortho-acid by repeatedly evaporating down with hydrochloric acid, and estimating by magnesia. To estimate the bases, the filtrate from the first silver precipitate was treated with prussic acid; the filtrate evaporated to dryness, and the mixed nitrates heated with kieselguhr. In other experiments, hydrochloric acid was used to remove silver, and the filtrate evaporated with sulphuric acid; the barium sulphate finally obtained, however, contained a little lithium, even after prolonged washing. Or, the liquid freed from silver by hydrochloric acid was evaporated with hydrochloric acid several times, so as to

convert the nitrates into chlorides, and then the chlorine in the mixture determined.

Analogous results were obtained when potassium pyrophosphate was substituted for the sodium salt: thus, equal molecule-weights of pyrophosphate and lithium chloride gave the compound $Li_3KP_2O_7$, or $3Li_2O.K_2O.2P_2O_5$, with 18·87 per cent. of water ($3H_2O$). Five molecules of lithium salt to 1 of pyrophosphate, gave a less crystalline salt, containing more lithium and less potassium; as the pyrophosphate used contained a little meta-phosphate, it is probable that these crystals were essentially lithium pyrophosphate, $Li_4P_2O_7$. These salts gave a violet blowpipe-flame, soon becoming pure crimson-red.

C. R. A. W.

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## The Chemical Constitution of Bleaching Powder.

By C. STAHLSCHMIDT (Dingl. polyt. J., ccxxi, 243—250).

THE author has expressed the view that chloride of lime may be considered as a calcium hydrate, in which 1 atom of hydrogen is replaced by chlorine; and further, that in the formation of chloride of lime, calcium chloride and water are produced; also that on bringing it in contact with water it splits up into calcium hypochlorite and hydrate:—

$$(1.)\ 3CaH_2O_2 + 4Cl = 2CaHClO_2 + CaCl_2 + 2H_2O.$$
$$(2.)\ 2CaHClO_2 + \text{Water} = CaCl_2O_2 + CaH_2O_2.$$

Experiments led to verification of the results of Graham, Bolley, Tschigianjanz, Fricke, and Reimer, that some calcium hydrates, dried at 100°, absorbed scarcely any chlorine, whereas others under the same conditions yielded good products. Dried over sulphuric acid, the limes absorbed chlorine readily. In the latter cases, however, it is considered that a small quantity of water is still present in the hydrate, which is a necessary condition for the absorption of the gas. 0·4 per cent. of water or more in the hydrate is sufficient, so that chloride of lime may be formed at 0°, but if the hydrate has been dried at 100° to 130°, it cannot be converted into chloride of lime, unless the latter undergoes a rise in temperature. In his experiments the author worked upon quite pure materials, and with scientific exactness. A low temperature was found to be unfavourable to the formation of chloride of lime, or at least to impede it. It was found difficult to account for the indisposition of certain limes to absorb chlorine gas. A calcium hydrate with a slight excess of free water, gave a chloride of lime no stronger than when a dry hydrate was used, but the former, under favourable conditions, might be made to absorb more chlorine, and finally attain a strength indicated by 39 per cent. of available chlorine. It was also found that a quick-lime, which slaked with difficulty, is less to be recommended for chloride of lime manufacture than one which slakes quickly. A lime of the former description absorbed the chlorine much more slowly, and gave a chloride of lime of only 31 to 35 per cent.

The following formula represents the formation of chloride of lime as bearing out the experimental results obtained:—

$$3CaH_2O_2 + 4Cl = 2CaHClO_2 + CaCl_2 + 2H_2O.$$

That water was liberated from perfectly dry calcium hydrate, on treatment with chlorine, was made manifest by the drops of water collected in the inlet-tube. In certain cases a chloride of lime is obtained containing upwards of 40 per cent. of chlorine. Göpner, by passing the chlorine through warm water of 60° to 70°, obtained a chloride of lime of 40·2, and another of 42·84 per cent. The author accounts for this as follows:—In presence of moisture a portion of the compound $2CaHClO_2$ in the already formed chloride is decomposed into $CaCl_2O_2$ and $CaH_2O_2$, the latter in presence of more chlorine, then giving $CaHClO_2$. The following reaction may also take place, $2CaH_2O_2 + 4Cl = CaCl_2O_2 + CaCl_2 + 2H_2O$, and when we have the two results, $2CaHClO_2 + CaCl_2 + 2H_2O$ and $CaCl_2O_2 + CaCl_2 + 2H_2O$, the strength of equal parts of such a mixture (chloride of lime) would be 43·5 per cent. actual chlorine; in the proportion of 5 : 1 = 40·5 per cent., and in that of 10 : 1 = 40·0 per cent. It is concluded that, with the help of the water liberated from the dry hydrate in its conversion into chloride of lime, together with that contained in, and carried along with the chlorine gas, the already described decompositions of the chloride of lime may take place, so that the amount of actual chlorine in the product will rise. This view is supported by the fact that in a manufactured sample of chloride of lime, prepared from calcium hydrate which contained about 8 per cent. of water in excess, besides the compound $CaClHO_2$, also calcium hypochlorite occurs in varying quantities. On suspending calcium hydrate in water, and passing a current of chlorine through the mixture, till alkalinity disappeared, and all the lime had dissolved, it was found that the following equation was exactly realised:—$2CaH_2O_2 + 4Cl = CaCl_2O_2 + CaCl_2 + 2H_2O$. This was proved by estimating in equal volumes of the solution, first the actual chlorine, secondly the lime. Of course the most conclusive proof of the existence of calcium hypochlorite in the chloride of lime solutions, is that Kingzett has obtained crystals of calcium hypochlorite from such solutions by evaporation, in a vacuum over sulphuric acid, or by cooling a concentrated solution below 0°. J. Kolb has observed that carbonic acid decomposes chloride of lime, liberating hypochlorous acid and leaving calcium carbonate. The author has had a sample of chloride of lime, which was thus reduced from 25 per cent. to 7 per cent. actual chlorine, the amount of calcium carbonate having risen to over 40 per cent.

The workmen can distinguish the hypochlorous acid from the chlorine by the slower action which the former exerts upon the lungs, and by its sweetish taste.

W. S.

**Electric and Chemical Deportment of Argentic Sulphide.** By W. Skey (Trans. and Proc. of the New Zealand Institute, 1876, 345—346).

It was stated by the author, in a former paper on the conducting power of sulphides, that argentic sulphide is a good conductor of electricity for a sulphide. The deportment of this substance to electric currents has since then given rise to some controversy, and

the results, as published by the author, have been found to leave a uniform impression upon chemists that this sulphide is not an electric conductor in the sense in which this term is usually and properly taken, *i.e.*, not a conductor as a metal is without decomposition. Thus Faraday supposed that it conducts electricity like a metal without decomposition, its conducting power, however, increasing with rise of temperature; while Hittorf is said to have shown that when this compound is free from metallic silver, it conducts only in proportion as it is decomposed.

In repeating his experiments the author found that by taking three plates of pure silver, which had been thickly coated with sulphide, placing them gently on each other, and connecting the outside ones with a feeble battery of one cell attached to a galvanometer, an electric current was still indicated, and was not notably less in quantity, than that which was indicated when these plates were out of the circuit. The same result followed at 300° F.

Regarding the chemical deportment of this substance, it was found, contrary to what is alleged respecting it, that it is soluble in potassium cyanide at ordinary temperatures. The same may be said with regard to auric sulphide. Platinic sulphide appears scarcely soluble in this salt. It was further noticed that it is not, as heretofore supposed, unattacked by mercury, but is slowly decomposed. The same is observed with auric sulphide. Galena is not decomposed. Argentic sulphide is further decomposed by cupric chloride alone, without the presence of an alkaline chloride.

D. B.

## Action of Halogen Acids on Tellurous Oxide. By A. Ditte (Compt. rend. lxxxiii, 446—448).

1. *Tellurous Oxide and Hydrobromic Acid.*—When gaseous hydrobromic acid is passed over tellurous oxide, it is absorbed, and a dark brown compound is produced, while the heat evolved is so great that it is necessary to cool the vessel containing the tellurous oxide to prevent partial decomposition. If the operation is carried on at a temperature of 15° C., the absorption ceases when the amount of hydrobromic acid absorbed is a little more than one equivalent. The tellurous oxide is transformed into a mass of dark brown tables, which, if the temperature is reduced to −14°, absorb a further quantity of hydrobromic acid, and agglomerate into small, dark brown, almost black masses of small plates resembling iodine, into which the gas passes with difficulty, so that it takes some time to finish the operation: the substance has then the following composition:—

| | Found. | Calculated. |
|---|---|---|
| $TeO_2$ ..... | 40·21 | 39·61 |
| HBr ..... | 59·79 | 60·39 |
| | 100·00 | 100·00 |

corresponding with the formula $TeO_2.3HBr$. No further absorption of hydrobromic acid takes place at −14°.

The compound $TeO_2.3HBr$ is decomposed at 40°, with production of a new substance, stable at that temperature; it contains:—

| | Found. | Calculated. |
|---|---|---|
| $TeO_2$ ..... | 49·98 | 49·69 |
| HBr ..... | 50·02 | 50·31 |
| | 100·00 | 100·00 |

which gives the formula $TeO_2.2HBr$.

This body begins to decompose at 70°, giving off water, and at 300° all the water is driven off, and a faintly-yellow mass left, which is oxybromide of tellurium:—

$$TeO_2.2HBr = TeOBr_2 + H_2O.$$

This oxybromide, when heated, melts to a very dark liquid, giving off nearly black vapours, and crystallising on cooling in long brown needles. The vapour condenses in the cold parts of the tube in small crystals generally coloured yellow by bromine; and a foliated mass remains at the bottom of the tube, slightly volatile at a red heat, insoluble in water, soluble in nitric acid; it consists of fused tellurous oxide. The crystals, which are instantly decomposed by water, consist of tellurium tetrabromide, $TeBr_4$, which is produced by the decomposition of the oxybromide into tetrabromide and tellurous oxide,—

$$2(TeOBr_2) = TeBr_4 + TeO_2.$$

2. *Tellurous Oxide and Hydrofluoric Acid.*—Anhydrous hydrofluoric acid is absorbed by tellurous oxide, with disengagement of heat; the compound produced has not yet been studied.

3. *Tellurous Oxide and Hydriodic Acid.*—Hydriodic acid gas passed over tellurous oxide at ordinary temperatures, decomposes it with great evolution of heat; but at −15° the oxide absorbs the hydriodic acid and agglomerates together, so that the absorption becomes very slow; the author was unable to fix as much as one equivalent; the compound produced is decomposed as soon as the temperature rises, with production of tellurium iodide.

H. W.

## Absorption of Antimony and Arsenic from a Solution of their Oxides in Hydrochloric Acid by Charcoal. By W. Skey (Trans. and Proc. of the New Zealand Institute, 1876, 337—338).

In the Chemical News, March 27, 1868, the author showed that freshly prepared or ignited charcoal absorbs several substances from their aqueous or acid solutions. It was therefore proposed to use this substance for the purification of chemical reagents. Further investigations in this direction have proved that antimony and arsenic can be so largely removed by fresh charcoal from solutions of their oxides or chlorides in moderately strong hydrochloric acid (with a little tartaric acid in the case of antimony), that neither of them can be detected therein by Reinsch's test. Such charcoal does not give up any por-

tion of metal to solutions of potash, hence it is probable that charcoal would absorb either of these metals from alkaline solutions. When, however, it is placed in voltaic contact with zinc in hydrochloric acid, antimoniuretted or arseniuretted hydrogen is evolved.

D. B.

**Oxidation of Silver, Platinum, and Gold, and supposed Oxidation of Mercury by Oxygen in presence of Water.** By W. SKEY (Trans. and Proc. of the New Zealand Institute, 1876, 332—334, and 339—342).

THIS paper gives a series of experiments which were made with the view of ascertaining whether oxygen combines, like sulphur, with gold or platinum at an ordinary temperature. For the oxidation of these metals the "mercury test" was used, which is based upon the fact that mercury readily amalgamates with silver and platinum when in contact with them, but that if the minutest film of any substance intervenes between the two metals amalgamation is either retarded or prevented.

The following facts were ascertained with regard to silver:—(1.) Pure silver, when immersed for a few hours in pure water, does not amalgamate immediately. (2.) Such effect is not produced with rain or spring water. (3.) Silver modified by distilled water is brought back to the amalgamable state by contact for a short time with rain or spring water, also with acetic acid or ferrous sulphide, and by raising its temperature to 500° F. (4.) Electric currents are generated by silver in saline water free from chlorides, iodides or bromides. (5.) Silver does not pass into this non-amalgamable state in dry air. (6.) Spongy silver immersed in an aqueous solution of sodium chloride soon renders it very alkaline. (7.) Sunlight exerts no effect in any of the above reactions.

With regard to platinum it was found that on placing it in contact for a short time with distilled water (also ammoniated), with aqueous solutions of the alkalis, or their carbonates or chlorides, it passed to a non-amalgamable condition, while acids for the most part quickly restored it to its amalgamable state. Platinum also generates electric currents when paired with graphite in saline of alkaline solutions. The author thinks that platinum not only absorbs oxygen, but that this absorption is a chemical one, an oxide or a sub-oxide being formed.

The following are the results obtained with regard to gold:—(1.) After immersion for a few hours in spring water, or in water charged with any neutral salt, gold refuses to amalgamate when subsequently immersed in mercury. (2.) It is also brought into this condition when left in contact with distilled water for about eighteen hours, or with an aqueous solution of caustic or carbonated alkali or ammonia at their boiling points, or for a longer time when the solution is used at the ordinary temperature. (3.) Gold is also brought into this state, when ignited with a weak solution of sodium carbonate. (4.) Weak acetic or hydrochloric acid or ignition readily convert this non-amalgamable surface into a readily amalgamable one. (5.) Gold becomes rapidly non-amalgamable in silver nitrate or mercuric chloride,

also in weak sulphuric acid, or when fused with borax and potassium bisulphate.

It seems, therefore, tolerably certain that gold thus acted upon has been oxidised, and this either to a sub-oxide or to the purple oxide of gold. The author intends to investigate this subject further, but whatever may be the precise nature of the film thus induced upon gold, and of the reactions which result in the removal or alteration of this film, it is certain that films of this kind must cover the surfaces of a portion of our native gold and thus retard to a more or less extent its complete amalgamation when milled.

The only results the author has yet been able to obtain with mercury seem to show that it is oxidised under similar conditions. For instance, electric currents of some strength are generated by it in water containing a little sodium chloride, also in aqueous solutions of caustic or carbonated alkali; and as the only conceivable effect of these salts is to conduct the electricity thus generated, and so render it detectable, the author concludes that these currents are not originated by such salts, but by the oxidation of mercury.

In conclusion it is stated that the above chemical action of oxygen on metals may explain the origin of those electric currents which Becquerel obtained by immersing certain non-oxidisable metals in pure water, and which he attributes to "capillary affinity."

D. B.

**On certain Chemical Effects of Oxygenised Graphite and Platinum.** By W. Skey (Trans. and Proc. of the New Zealand Institute, 1876, 347—348).

It was found:—(1.) That any surface of graphite, native or artificial, which has been for some time exposed to the air, liberates iodine from a solution of potassium iodide in weak sulphuric acid. (2.) That graphite which can thus liberate iodine loses this property when washed with ammoniacal or other alkaline solutions, also by ignition. (3.) That this property of liberating iodine is restored to such graphite by a short exposure to the air, or by evolution of nascent hydrogen against it, also by digesting it for a little while with hydrochloric acid or weak sulphuric acid at an ordinary temperature or at the boiling point. (4.) That graphite which thus liberates iodine also rapidly determines a chemical effect upon mercury when voltaically paired with it in pure hydrochloric acid, mercurous chloride forming. (5.) That platinum can be substituted for graphite in the above experiments with the same results. (6.) That charcoal does not, even when freshly prepared, notably liberate iodine, but does so when digested with an acid, which perhaps effects the removal of all alkaline matters therefrom, and enables the charcoal to retain the oxidising agent necessary for effecting the liberation in view. (7.) That silver also liberates iodine from its solution, and gold also does this, though to a much less extent: and (8) that nitric acid has the same effect upon graphite or platinum as exposure to the air, and that prolonged washing of these metals afterwards does not in any way inter-

fere with this effect, showing no doubt that the acid has been absorbed by these metals and is retained very obstinately.

The author intends to supplement the above results in such a way as will enable him to discriminate with greater surety than he can at present, the exact nature of the absorptive process by which graphite and platinum become chemically active in the way indicated by these results.

D. B.

# Mineralogical Chemistry.

## Mineralogical Notes. By F. PISANI (Compt. rend., lxxxiii, 166).

*Amesite.*—This name was given by Shepard to a mineral found on some diaspore at Chester (Mass.). It occurs in small crystalline masses, formed of superposed layers, of hexagonal appearance, with easy cleavage parallel to the base, accompanied by scattered needles of rutile. Translucent in thin plates. A thin plate exhibits a positive optic axis with the polarising microscope. Lustre pearly. Colour pale apple-green. Hardness 2·5 to 3. Density 2·71. Before the blowpipe it becomes blackish and is almost infusible. Composition:—

| $SiO_2$. | $Al_2O_3$. | FeO. | MgO. | $H_2O$. |
|---|---|---|---|---|
| 22·40 | 32·30 | 15·80 | 19·90 | 10·90 |

*Euchlorite.*—A magnesian mica, found in schistose masses, formed of scales having an easy cleavage parallel to the base. Translucent in thin plates. With the polarising microscope it exhibits a single negative axis, across the base. Colour deep green. Somewhat flexible. Hardness 2·5. Density 2·84. Composition:—

| $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | MgO. | Alkalis. | Loss on ignition. |
|---|---|---|---|---|---|
| 39·55 | 15·95 | 7·80 | 22·25 | 10·35 | 4·10 |

*Spessartine.*—An extremely pure variety of garnet, generally light yellow in colour; rarely orange. Found at Saint Marcel, chiefly as a crystalline incrustation, exhibiting the faces $b^1$ $a^2$, the rhombic dodecahedron being predominant, on a centre or kernel of marceline or braunite.

*Bastite.*—Some specimens of this mineral were received from the Island of Elba. They in every way resembled the specimens examined by Des Cloiseaux from Baste, belonging to the orthorhombic system.

C. H. P.

## Microline Felspar and Andesite.

By CH. ST. CLAIRE DEVILLE (Comptes rendus, lxxxii, 1015).

THE discovery of microline (a triclinic felspar with potassic base), described by Des Cloiseaux in a recent number of the *Comptes rendus*, establishes the connection between the felspars, such as orthose characterised by a predominance of potassium, and albite characterised by a predominance of sodium; minerals which, while possessing the same numerical formula, 1 : 3 : 12, representing the oxygen of the protoxide, the oxygen of the sesquioxide, and the oxygen of the silica, crystallise in two incompatible forms. The potassium is then the *pivot*, or connecting link common to the two minerals; and since in amphigene (1 : 3 : 8) potassium is the predominant base, the potassium must be the connecting link between the felspars and the amphigenes, in the same way as calcium is common to both anorthite and certain varieties of sarcolite, both having the numerical formula (1 : 3 : 4), but being of different mineralogical forms.

C. H. P.

## Microscopical Examination of Orthose and of sundry Triclinic Felspars.

By A. DES CLOISEAUX (Compt. rend., lxxxii, 1017—1022).

IN a previous paper the determination of the almost constant angle, which the direction of the maximum extinction of the polarised ray makes with the side $p.\ g^1$, was insisted upon as a characteristic of microline in all the specimens cut into excessively thin plates, in the direction of their two principal cleavages $p$ and $g$. Having tried whether the application of this method could be used for the immediate distinction from one another of the known felspars of the triclinic system, the author states that occasionally some hesitation may arise in the discrimination between certain laminar samples of albite and labradorite; and in those cases it is better to determine the rotation and the dispersion of the optic axes, as explained in the *Annales de Chimie. et de Physique*, vol. iv, for 1875.*

The varieties of orthose may be divided into two categories; the one, the pure specimens which exhibit in very thin plates parallel to $p$ and $g$, a structure whose homogeneity is affected only by very slight inclusions of foreign bodies; the other, the specimens penetrated with albite in more or less abundant veins and of which the most regular type is the *perthite* of Canada.

A list of those varieties of orthose which are ranged in each of these two catagories is then given, and the consideration of the angular measurements which the line of the plane of maximum extinction makes with the side $p\ g$, for albite, oligoclase, labradorite, and anorthite, as determined on a variety of specimens, follows.

C. H. P.

* See also this Journal, 1875, p. 741.

**A Nickeliferous Mineral in Spain.** By M. MEISSONNIER (Compt. rend., lxxxiii, 229).

IN the province of Malaga a mineral has been discovered in which nickel occurs in the form of silicate, as in the ore met with in New Caledonia. The absence of arsenic and antimony allows the extraction of a very malleable and easily wrought metal, much superior to the products of the German mines, and the working of the new ore has been recently commenced. The mineral contains about 9 per cent. of nickel, and no cobalt.

R. R.

**Olivine-rock, Serpentine and Eclogite of the Saxon Granulite District (conclusion).** By E. DATHE (Jahrb. f. Min., 1876, 337—357).

II. *Bronzite Serpentine.*—Large masses of serpentine-rock occur at Kuhschnappel, Langenberg, and Callenberg, between granulite-rock and mica-schist. They are characterised by a predominating dull black or dark brown colour; very few appearing of a light green colour. A macroscopical examination revealed the presence of crystal-laminæ having a brownish-yellow or brass-yellow lustre, which had the appearance of bronzite or enstatite. A chemical analysis proved these crystalline masses to be one of the above-mentioned minerals. Light-green or greyish-white, round, hexagonal crystals, having a fibrous structure, appeared to be a secondary product, probably bastite.

*Serpentine from Langenberg.*—This rock is of a dull black colour, and contains numerous brownish-black crystals of bronzite, which sometimes attain a length of 2 cm. A thin section of the rock shows these crystals to be built up of fine longitudinal fibres, being not uniform, but slightly undulating. The chief directions of elasticity are either parallel or at right angles to the striation, and optical examination proves the crystals to be rhombic. Small opaque needles occur in the bronzite parallel to the longitudinal fibre-formation or striation. Many of the bronzite masses are much decomposed, the resulting product being serpentine, whilst a thin film of ferric oxide is deposited in the striation. No residuum of olivine was observed in this rock, but from the presence of broad reticulated fibres of chrysotil, it is evident that the original rock must have contained a large amount of olivine. Small crystals of chromite were also observed.

*Serpentine near the Ziegelei between Russdorf and Mensdorf.*—Is leek-green in colour, and contains bastite as a secondary product after bronzite or enstatite. A very decided reticulated structure shows its origin from olivine. Chromite was also observed in this specimen.

*Serpentine from Callenberg.*—Is of a dirty green to brown colour, and contains numerous small bronzite individuals disseminated throughout the mass. No olivine could be detected, as the decomposition of the original rock was complete; but a decided reticulated structure was observed, and in the interior of each mesh, and perpendicular to it

was a broad plate of chrysotil. The bronzite was also much decomposed, exhibiting a fine fibre formation, so that it was partially converted into bastite. The author concludes his remarks upon the origin of serpentine by stating that it could not be derived from gabbro, as this rock is composed of plagioclase, diallagite, quartz and magnetite; most of which minerals are unfavourable to the formation of serpertine. There can, however, be no doubt (after a careful study of the results of his examinations of all the varieties of serpentine-rock given in his table of the serpentine of the Saxon granulite district) that it is derived from a bronzite-olivine rock.

III. *The Eclogites. Eclogite from above the Tunnel near Waldheim.*—Occurs as a layer, not quite one meter in thickness, between serpentine; granulite also occurs twice, alternating with serpentine. The chief constituent of the rock is augite, which is accompanied by pale red garnets, both evident upon macroscopic examination. The augite is of a light red colour, dichromatic, and the characteristic angle of prismatic cleavage, viz., 87° is also obtained. Hornblende often occurs intergrown with augite crystals, some of the latter being penetrated by irregular quartz-grains, whilst others are so darkly coloured by ferric oxide, that they have the appearance of magnesia-mica. The augite also is slightly decomposed, as in cracks and clefts of the same a light green or greyish pulverulent and sometimes radiating substance is observed, which may be viridite. Magnetite in a finely divided state is also observed. The garnet occurs equally distributed with the augite, is of a pale red colour and seldom encloses other minerals, the most common being well developed garnets and quartz crystals. In polarised light these quartz crystals (exhibiting the forms $\infty$ P and + R.) appear in the most vivid colours protruding from the dark garnet mass. Sometimes regular series of fluid enclosures and hollows are observed in the garnets; they are also decomposed, the product being fine, spiral, light green radiating fibres and laminæ, which probably belong to a mineral of the chloritic group. Magnesia-mica occurs occasionally as a constituent of the rock, also, partially as ground-mass, plagioclase and quartz, and sparingly irregular distinct iron pyrites individuals.

*Eclogite from the Quarry at the Gebersbach, in Waldheim.*—This rock is coarse-grained and contains garnet, hornblende and porphyritic felspar. Magnesia-mica often occurs intergrown with the hornblende in various directions, and is easily distinguished from the latter by its very decided dichroïsm (brown to black), whilst the hornblende resembles closely in colour and texture the anthophyllite of Bodenmais, and often encloses opaque needles and grains. The garnet is mostly decomposed, as green laminæ are observed grouped round the garnet residue, evidently consisting of chloritic substance, and at the same time of magnesia-mica. There is a large deposit of magnetite occurring between the green laminæ. Triclinic felspars are very prominent, whilst quartz grains and small plagioclases are occasionally enclosed by the large felspar crystals. Iron-pyrites was observed macroscopically.

*Eclogite from the Quarry in Greifendorf and from the Bohrberg near Böhrigen.*—R. von Drasche (*Tschermak's Min. Mitth.*, 1871, ii, 90)

described eclogite from the first named locality, and pointed out the presence of hornblende surrounding the garnet crystals. The author considers (contrary to the opinion of Weigand) that the former was derived from the latter, and by treating a thin section for several hours with hot sulphuric acid, proved that the so-called hornblende was undoubtedly a chloritic mineral, as the green laminæ surrounding the garnets were bleached and attacked, and covered with silica, which had separated out, whilst the brown hornblende was scarcely altered in appearance. The green laminæ were dichromatic, light green to dark green, and may either be ripidolite or clinochlor. Well developed crystals of quartz ($\infty$ P. $\pm$ R.) occur enclosed in the undecomposed garnet substance, also smaller garnets and magnetite. Plagioclastic felspar occurs sparingly in the eclogite from Greifendorf, but it predominates in the rock from Bohrberg, also large black spots of iron-pyrites and some small zircon crystals. The eclogite from the valley near Gilsberg has a similar composition, and the author concludes, from the results of his examinations of the eclogite of the Saxon granulite district, that augite and hornblende (either singly or together), garnet, plagioclastic felspar and quartz are natural constituents of the rock; magnesia-mica and iron pyrites are accessory minerals; and chlorite and magnetite secondary products. The only exception to the rocks having the above-mentioned composition is the eclogite from behind the restaurant "zur Erholung" in Waldheim, it being exclusively built up of light green augite and pale rose-red garnet; the former being decomposed into viridite and pistazite, and the latter being surrounded with chlorite laminæ. From the position of the eclogite in the serpentine, and the trifling thickness of the bed of the Gebersbach quarry from above the tunnel of Waldheim, Dathe is of opinion that serpentine is not derived from eclogite, and that the latter was formed simultaneously with the original rock from which the serpentine was derived.

C. A. B.

## Presence of Nickel in Atmospheric Dust.

By G. TISSANDIER (Compt. rend., lxxxiii, 75—78).

FERRUGINOUS particles separated by the magnet from the sediment of rain-water, and from dust falling direct from the air, were found to contain distinct traces of nickel. Microscopic examination of the particles showed them to be very various in form. Some were very black and amorphous; some consisted of compact granular accretions; whilst others of larger dimensions had rugose or mammillary surfaces. The author believes the particles to be meteoric.

J. R.

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## Carbon-compounds in Meteorites. By J. LAWRENCE SMITH (Compt. rend., lxxxii, 1041).

THE memoir contains an account of the author's researches on a crystallisable sulphuretted hydrocarbon, the discovery of which in the graphitic nodules of meteoric irons he recently announced. He like-

wise indicates how he found the same body as well as other compounds of carbon, on the black or carboniferous meteorites.

Mention is also made of another sulphuretted hydrocarbon in the residues of the meteorites, which body is odourless when dry, but exhales the odour of assafœtida when wetted. These sulphuretted bodies were too small in quantity to permit of a thorough determination of their nature.

C. H. P.

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## Carbon-compounds found in Meteorites.

By J. LAWRENCE SMITH (Compt. rend., lxxxii, 1507).

THE author has pursued his investigations on the crystallisable hydrocarbons originating from terrestrial irons and doubtful meteorites like that of Ovifak (which contains a very considerable proportion of this carbon). In these irons a substance was found similar to that which occurs in meteoric graphite, and in carbonaceous meteorites it has the same strong smell, and crystallises in small needles, melts rapidly when heated on a platinum spatula, and when heated more strongly, burns with a flame and volatilises completely. When heated in a tube it volatilises to some extent and condenses on the cold parts of the tube, leaving a residue of carbon. The author cannot yet say with certainty whether these new bodies are identical with those obtained from the meteorites recently described.

D. B.

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## Note on a Meteorite which fell on March 25, 1865, at Wisconsin, and is Identical in Character with the Meteorite of Meno.

By J. L. SMITH (Compt. rend., lxxxiii, 161).

THE meteorite of Meno fell on October 1st, 1861, and its similarity of composition to that which fell in Wisconsin on March 25th, 1865, is shown by the following analyses:—

| | Wisconsin. | Meno. |
|---|---|---|
| Stony matter | 78·33 | 77·76 |
| Metallic „ | 17·07 | 18·00 |
| Troïlite | 4·60 | 4·24 |
| | 100·00 | 100·00 |
| Stony matter, soluble | 47·2 | 48·7 |
| „ „ insoluble | 52·8 | 51·3 |
| | 100·0 | 100·0 |
| Stony matter— | | |
| Silica | 44·98 | 44·70 |
| Ferrous oxide and alumina | 21·95 | 22·26 |
| Magnesia | 29·30 | 28·97 |
| Lime | 1·80 | 1·85 |
| Soda | 1·32 | 1·20 |

Metallic matter—

| | Wisconsin. | Meno. |
|---|---|---|
| Iron | 91·15 | 91·86 |
| Nickel | 7·37 | 7·53 |
| Cobalt | 0·28 | 0·15 |
| Copper and phosphorus | traces | traces |
| Sp. gravity | 3·66 | 3·65 |

C. H. P.

# Organic Chemistry.

## Absorption of Nitrogen and of Hydrogen by Organic Matters. By BERTHELOT (Compt. rend., lxxxii, 1357—1360).

UNDER the influence of the silent electric discharge, nitrogen gas, whether pure or mixed with oxygen, is absorbed by such organic matters as moist filtering paper, and solution of dextrin, to an extent which in the course of a few hours, is very notable. Fixed complex nitrogenous compounds are the products of the reactions; but neither ammonia, nor any acid of nitrogen, is formed under the conditions of the experiments. Thus it appears that the fixation of nitrogen may take place in nature, without any preliminary formation of ozone, ammonia, or nitrous compounds.

Under like conditions, hydrogen gas is even more readily absorbed by certain substances. Thus 1 c.c. of benzene will take up 250 c.c. of hydrogen, and turpentine also absorbs the gas freely. Acetylene mixed with hydrogen, besides yielding the condensation-products, as in Thénard's experiments, causes the disappearance of a certain quantity of hydrogen. The products in these cases appear to consist of various polymeric and other bodies. The electrified hydrogen had no action on pure carbon; but a mixture of carbonic oxide and hydrogen gave rise to a solid product and carbonic acid, besides which the author detected a trace of acetylene, and of some formenic carbide.

R. R.

## Absorption of Hydrogen under the Influence of the Dark Discharge. By BERTHELOT (Bull. Soc. Chim. [2], xxvi, 98—100).

ONE molecule of benzene absorbs nearly two atoms of hydrogen, and yields a polymeride of $C_6H_8$, which is a resinous body having a strong and disagreeable smell. It froths up on heating without melting, and decomposes. First, a little benzene distils over, then a liquid which completely dissolves in fuming nitric acid and in fuming sulphuric acid, forming a sulphonic acid. Afterwards a thick liquid passes over, and carbon containing hydrogen remains behind.

Oil of turpentine absorbs 2·5 atoms of hydrogen, and forms resinous

products. When it is submitted to the dark discharge in presence of water, no hydrate is formed.

*Pure* carbon does not combine with hydrogen. A mixture of acetylene and hydrogen behaves almost like pure acetylene, but some of the hydrogen, about one-fifth of that of the acetylene, disappears. The product $(C_2H_2)_n$, which Thénard obtained from pure acetylene, decomposes quickly and with the evolution of heat on heating it in an atmosphere of nitrogen, yielding a little styrolene, a tarry hydrocarbon, a residue of carbon containing hydrogen, and a gaseous mixture consisting of—

| | |
|---|---|
| Acetylene | 4 |
| Ethene | 8 |
| Crotonylene | 20 |
| Ethane | 14 |
| Hydrogen | 54 |
| | 100 |

The volume of this mixture is only 2 per cent. of that of the original acetylene.

A mixture of hydrogen and carbon monoxide yields the solid body, which was observed by Brodie and by Thénard, and is formed according to the equation—

$$5CO + 3H_2 = CO_2 + C_4H_6O_3.$$

Besides these compounds a trace of acetylene is formed, and another gas, which is either marsh-gas, or more probably a mixture of equal volumes of ethane and hydrogen.

Carbon dioxide and marsh-gas form not only the caramel-like body which Thénard observed, but also a trace of butyric acid, while the gaseous residue contains a little acetylene, and much carbon monoxide.

C. S.

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**A New Method of Substituting Chlorine and Bromine in Organic Compounds.** By O. DAMOISEAU (Compt. rend., lxxxiii, 60—62).

MANY substances which under ordinary circumstances are not affected by chlorine and bromine, even at elevated temperatures, are readily attacked by them in presence of animal charcoal. By means of this substance most of the reactions which have hitherto been found possible under the influence of light only may be very easily effected. The best form of charcoal for the purpose is that obtained by calcining a mixture of dried blood and potassium carbonate. It should be carefully washed, and re-calcined at as high a temperature as possible.

A mixture of chlorine and ethyl chloride, passed through a tube containing such charcoal, and heated to 250—400°, is transformed into hydrogen chloride and one or more of the chlorinated derivatives of ethyl chloride, any of which may be obtained almost pure by properly regulating the proportions of the gases employed. Carbon trichloride, $C_2Cl_6$, may thus be prepared easily and cheaply.

Ethylene is similarly acted on by chlorine under the same circumstances.

The brominated derivatives of ethylene bromide and ethyl bromide, up to $C_2Br_6$, are readily obtained by the same means. In order to obtain any of these derivatives singly, the author finds it best to dissolve the requisite quantity of bromine in ethylene or ethyl bromide, and to allow the mixture to fall drop by drop on the hot charcoal. Volatilisation of the two substances in the proper proportions is thus effected instantaneously.

J. R.

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## On Organo-boron Compounds. By E. Frankland (Proc. Roy. Soc., xxv, 165—168).

The author, in 1862 (*Phil. Trans.*, cliii, 167; this Journal, xv, 363), described the action of zinc-ethyl and zinc-methyl on triethylic borate (boric ether), and showed that these organo-metallic bodies displace the ethoxyl ($OC_2H_5$) by the organic radicle which they contain. Thus:—

$$\underset{\text{Boric ether.}}{B(OC_2H_5)_3} + \underset{\text{Zinc-methyl.}}{3Zn(CH_3)_2} = \underset{\text{Boric methide.}}{B(CH_3)_3} + \underset{\text{Zinc methethylate.}}{3Zn\left\langle\begin{matrix}CH_3\\OC_2H_5\end{matrix}\right.};$$

Further, that boric ethide, when cautiously exposed to a slow current, first of air and then of dry oxygen, takes up 2 at. oxygen, forming boric etho-diethylate $(C_2H_5)B(OC_2H_5)_2$, a liquid boiling with partial decomposition between 95° and 125°, but distilling unchanged under reduced pressure. By contact with water this compound is instantly changed into boric ethodihydrate $(C_2H_5)B(OH)_2$. Thus:—

$$(C_2H_5)B(OC_2H_5)_2 + 2H_2O = 2C_2H_5OH + (C_2H_5)B(OH)_2.$$

Further experiments on these compounds have led to the following results:—

*Boric ethide* may be prepared by passing a current of the vapour of boric chloride through zinc-ethyl—

$$3Zn(C_2H_5)_2 + BCl_3 = B(C_2H_5)_3 + 3Zn\left\langle\begin{matrix}C_2H_5\\Cl\end{matrix}\right..$$

*Boric ethopentethylate*, $B_2(C_2H_5)(OC_2H_5)_5$, is formed by heating 2 molecules of boric ether with 1 molecule of zinc-ethyl—

$$2B(OC_2H_5)_3 + Zn(C_2H_5)_2 = Zn(C_2H_5)(OC_2H_5) + B_2(C_2H_5)(OC_2H_5)_5.$$

It is a colourless, mobile liquid, boiling at about 112°, and condensing without alteration. Its vapour-density, taken between 114° and 120°, is 69 (H = 1), which represents a 4-volume condensation, indicating that the compound, in passing from the liquid to the gaseous

state, is broken up into boric ethodiethylate and boric triethylate—a triethylic borate—

$$B_2(C_2H_5)(OC_2H_5)_5 = (C_2H_5)B(OC_2H_5)_2 + B(OC_2H_5)_3.$$

A similar deportment is exhibited by ammonio-boric methide, $NH_3.B(CH_3)_3$ (described in the author's former paper) which is resolved by heat into $NH_3$ and $B(CH_3)_3$, the mixed vapour resulting from the decomposition having also a 4-volume condensation. These decompositions, which are similar to that of sal-ammoniac, $NH_4Cl$, into $NH_3$ and HCl, which together occupy 4 volumes of vapour, render it probable that the compounds under consideration have a constitution analogous to that of the ammonium-salts, and that boron, though usually triadic, may, like nitrogen, enter into combination as a pentad. On this view the constitution of ammonio-boric methide and diboric ethopentethylate may be represented by the following formulæ:—

$$\begin{array}{c} NH_3 \\ || \\ B(CH_3)_3 \end{array} \qquad\qquad \begin{array}{c} (C_2H_5)B(OC_2H_5)_2 \\ || \\ B(OC_2H_5)_3 \end{array}.$$

Ammonio-boric methide. Diboric ethopentethylate.

*Boric diethoethylate* $(C_2H_5)_2B(OC_2H_5)$, intermediate between boric ethide and boric ethodiethylate, is formed in large quantity by boiling boric ether with 2 molecules of zinc-ethyl.

$$B(OC_2H_5)_3 + 2Zn(C_2H_5)_2 = 2Zn\begin{array}{l} C_2H_5 \\ OC_2H_5 \end{array} + (C_2H_5)_2B(OC_2H_5).$$

When thus prepared it retains a small quantity of boric ethylate or of diboric ethopentethylate, from which it cannot be freed even by repeated rectification. It may, however, be obtained pure by distilling diboric ethopentethylate, with 3 molecules of zinc-ethyl, in an atmosphere of carbonic anhydride:—

$$B_2(C_2H_5)(OC_2H_5)_5 + 3Zn(C_2H_5)_2 = 3Zn\begin{array}{l} C_2H_5 \\ OC_2H_5 \end{array} + 2(C_2H_5)_2B(OC_2H_5).$$

This product, when rectified, is a colourless, mobile liquid, having an ethereal odour and pungent taste, boiling at 102°, distilling unchanged, and having (at 135·5°) a vapour density of 56·5 (H = 1). indicating a normal 2-volume condensation. It takes fire in the air, and burns with a greenish flame. Exposed to dry air, and then to oxygen, it oxidises to boric ethodiethylate—

$$(C_2H_5)_2B(OC_2H_5) + O = (C_2H_5)B(OC_2H_5)_2.$$

*Boric diethohydrate* $(C_2H_5)_2B(OH)$, formed by agitating boric diethoethylate with water, is a spontaneously inflammable ethereal liquid, which resembles boric ethide, and is decomposed on distillation.

*Boric etho-ethylate-hydrate*, $(C_2H_5)B\begin{cases}OC_2H_5\\OH\end{cases}$, is formed by exposing boric dietho-hydrate in a cooled vessel to a slow current of dry air. It is liquid at ordinary temperatures, but solidifies below 8° to a white crystalline body, smelling like boric ethide, and having a pungent taste. It is rapidly decomposed by water into alcohol and boric ethodihydrate, according to the equation—

$$(C_2H_5)B\begin{cases}OC_2H_5\\OH\end{cases} + H_2O = C_2H_5OH + (C_2H_5)B(OH)_2.$$

It is not spontaneously inflammable, and cannot be distilled under ordinary atmospheric pressure without decomposition.

H. W.

**Constitution of the Propylene Chlorhydrins, and Law of Addition of Hypochlorous Acid.** By L. HENRY (Compt. rend., lxxxii, 1266—1268).

THE evidence brought forward by the author respecting the law of addition of hypochlorous acid, and the constitution of the propylene chlorhydrins not having convinced Markownikoff that the views he holds are in reality incompatible with experimental facts, additional evidence is now advanced, confirming the author's previous communications. According to Henry, the oxidation of the chlorhydrin obtained by the addition of propylene to hypochlorous acid, results in the formation of chloro-propionic acid, which has been further identified with the acid obtained from ordinary lactic acid. According to Markownikoff, acetic acid is the principal resultant of the oxidation; hence the difference in their views respecting the constitution of the chlorhydrin.

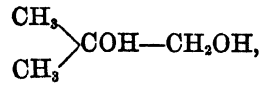
The author shows that the discrepant observations are due to the use of different oxidising agents; when chromic acid is used, chloropropionic acid results, but when nitric acid is substituted, the chloropropionic acid is broken up, and hydrochloric, carbonic, oxalic, and acetic acids obtained. The formation of oxalic acid by both methods of oxidation, does not favour Markownikoff's view, since it is well known that this acid is invariably a product of the oxidation of tricarbon compounds.

It may be, therefore, considered as settled that the constitution of the chlorhydrin is proved by the formation of monochloro-propionic acid, that it is, in fact, the primary, and not the secondary chloro-alcohol, having for its formula $CH_3—CHCl—CH_2.OH$. The compound, therefore, obtained by Markownikoff in its oxidation, must have been chloropropylic aldehyde, and not the corresponding chloro-acetone.

J. W.

## A New Butyl Glycol. By M. Nevole (Compt. rend., lxxxiii, 65—67 and 146—148).

The author has obtained the tertiary butyl glycol,



by the following process:—Butyl alcohol of fermentation was converted into butyl bromide by the action of hydrogen bromide. The bromide, when treated with alcoholic potash, yielded a butylene which combined with bromine to form a dibromide boiling at 147—148°. From this last, the glycol was obtained by heating it with potassium carbonate for 10 days. The yield was very small.

The glycol boils at 176—178°. Its sp. gr. is 1·0129 at 0°, and 1·0003 at 20°. It dissolves freely in alcohol and water. In a mixture of solid carbon dioxide and ether, it solidifies to an amorphous transparent mass. Potassium permanganate, in dilute aqueous solution, oxidises it to acetic and carbonic acids. Nitric and chromic acids form other oxidation-products, which have not yet been sufficiently examined.

J. R.

## Paraldol, a Polymeric Modification of Aldol. By Ad. Wurtz (Compt. rend., lxxxiii, 255—256).

When aldol is allowed to stand for some weeks, crystals are formed, which may be separated from the portion that remains fluid by washing with ether. This substance has the same percentage composition as aldol, and bears the same relation to it as paraldehyde does to aldehyde. The author has named it *paraldol*. It softens at 80°, and distils *in vacuo* between 90° and 100°. It is easily soluble in water, and also in alcohol; 1 part of paraldol dissolves in 3·8 parts of alcohol at 99°. From that solvent, it crystallises in anorthic prisms. It dissolves in 20 times its weight of ether at 23°, and crystallises from the solution, but the last portions of the mother-liquid contain aldol, produced apparently from the paraldol. Silver oxide transforms it into γ-oxybutyrate, like aldol itself. Crystallographic measurements are given.

W. R.

## Decomposition of Chloral Hydrate by Heat. By Alex. Naumann (Deut. Chem. Ges. Ber., ix, 822).

Determinations of the density of the vapour given off by chloral hydrate in Hofmann's apparatus, gave the following values:—

| | | |
|---|---|---|
| Alcohol vapour used (temp. = 78·5°).... | density | 2·81 |
| Water „ „ 100° .... | „ | 2·83 |

The formula $C_2H_3Cl_3O$ represents a density of 5·72, whilst the mixture of vapours, $C_2HCl_3O + H_2O$, corresponds to 2·86.

Hence chloral hydrate does not volatilise unchanged, but splits up into two bodies even at 78°, being in this respect analogous to ammonium carbamate. On cooling, liquid striæ condense, but do not begin to crystallise till the temperature falls below 40°.

Excess of chloral hydrate in a given space forms a vapour having a tension of 1·5 to 3·0 mm. at 6° to 14°; at 20°, the tension is under 6 mm., the same value being arrived at by cooling the vapour after continued heating to 35°.

At higher temperatures, *e.g.*, the temperature of boiling ether, carbon disulphide, and alcohol (35°, 46°, and 78° respectively), chloral hydrate does not exhibit a constant vapour-tension, even after some considerable time; thus, at 35°, four consecutive readings, each 10 minutes apart, gave tensions rising regularly from 11·5 (after the first 10 minutes) to 16 mm. (after the last 10 minutes); whilst in another set of four readings every 15 minutes, the tensions rose from 12·5 to 17 mm. Similarly, at 46°, 12 consecutive readings every 10 minutes gave values regularly increasing from 18 to 47·5 mm.; and at 78°, 3 readings gave the values 261, 284, and 296 mm.

C. R. A. W.

**Action of Warm Potash Solution on Glycogen.** By M. v. VINTSCHGAU and M. J. DIETL (Pflüger's Archiv. f. Physiologie, xiii, 253–267).

THE separation and estimation of glycogen in animal tissues has hitherto necessitated the boiling of the tissues in a potash solution. Although Bernard, Brücke, and Sigmund Weiss had asserted that the potash exercised no action on the glycogen, the authors, being about to experiment on glycogen, considered it advisable to test the statement for themselves.

They prepared their glycogen from calves'-liver in the manner described in Brücke's *Lehrbuche der Physiologie*, 2 ed., vol. i, p. 319, and obtained a specimen absolutely free from nitrogen, and containing only 0·12 per cent. of ash.

In experimenting, a definite quantity of the glycogen was dissolved in water and heated with potash solution of known strength to a given temperature for a given time. The solution was then rapidly cooled in water at 0° C., slightly acidified with hydrochloric acid, and the glycogen precipitated by alcohol.

The greater part of the precipitate having been thrown on a weighed filter, the remainder was dissolved in water and reprecipitated with alcohol. The precipitates were dried at 100°, subsequently at 110°, and sometimes to 130—140°.

A systematic series of experiments has led the authors to the following conclusions. Glycogen, when warmed with a very dilute solution of potash, *i.e.*, containing 0·04—0·06 per cent., so long as the temperature does not reach the boiling point, suffers an increase in weight, which increase is less the nearer the temperature approaches to the boiling point. If, however, the liquid be boiled, or the potash-solution concentrated, a loss is sustained. The more concentrated the potash-solution, or the longer the boiling is conducted, the greater the loss.

The maximum gain was 2·5 per cent., the maximum loss, 11·7 per cent.

The losses obtained seem to point to the formation of a compound only partially precipitated by dilute alcohol.

F. J. L.

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**Trichlorobutyric Acid.** By KARL GARZAROLLI-THURNLAK (Liebig's Annalen, clxxxii, 181).

SO-CALLED "croton-chloral hydrate" (butyl-chloral hydrate), was dissolved in 2 parts of water and treated with chlorine gas, the liquid being heated in the water-bath; after some 30 hours, the greater part of the chloral ceased to crystallise out on cooling, a heavy oil being formed instead; the supernatant fluid was shaken with ether, and on evaporation of the ether a little more oil was regained. The total oil thus produced was washed with a little water and then treated with pure calcium carbonate: finally *trichlorobutyrate of calcium* was obtained.

The yield being but small with this method of operating, the butyl chloral was treated with nascent chlorine evolved from potassium chlorate and hydrochloric acid; in this way, an oil was obtained which solidified in a freezing mixture and gave calcium, lead, and ammonium salts, agreeing with the *trichlorobutyrates*, and containing more hydrogen than trichlorocrotonates.

Similarly, on treating the chloral with nitric acid, trichlorobutyric acid is formed, and not, as stated by Judson, trichlorocrotonic acid. Moreover, Judson describes the lead salt of the acid obtained in this way as containing 2 molecules of water of crystallisation; the author, however, finds it is anhydrous.

Hence the action of chlorine on butyl-chloral hydrate is—

$$C_4H_5Cl_3O.H_2O + Cl_2 = 2HCl + C_4H_5Cl_3O_2:$$

had the chloral been (as originally supposed by Kraemer and Pinner) croton chloral, tetrachlorobutyric acid must have resulted; thus—

$$C_4H_3Cl_3O.H_2O + Cl_2 = 2HCl + C_4H_3Cl_3O_2$$
$$C_4H_3Cl_3O_2 + HCl = C_4H_4Cl_4O_2,$$

*i.e.*, trichlorocrotonic acid would be first formed, and this would then take up the elements of hydrochloric acid.

Attempts to make the chloral unite with hydrochloric acid and form a tetrachlorinated body (which should result were the chloral really of the crotonic series) proved abortive.

On heating trichlorobutyric acid with caustic potash at 100° for several hours, a minute amount of a substance agreeing in properties with dichlorocrotonic acid was formed, apparently by the removal of the elements of hydrochloric acid.

C. R. A. W.

## Sulphodicarbonic Acids. By H. WELDE (Deut. Chem. Ges. Ber., ix, 1044—1048).

WHEN equivalent quantities of ethyl chlorocarbonate and potassium xanthate are mixed together, a reaction takes place resulting in the formation of a white precipitate and an oily liquid. The latter when treated with water yields a thick yellowish oil, which afterwards solidifies, and may be crystallised from alcohol in fine yellow needles melting at 55°. Its composition agrees with that of *ethyl disulphodicarbothionate*, and its formation may be represented thus:—

$$3CS^{OC_2H_5}_{SK} + 2CO^{OC_2H_5}_{Cl} = 2S^{CSOC_2H_5}_{CSOC_2H_5} + CO^{OC_2H_5}_{OK} + 2KCl.$$

The new body, when treated with alcoholic potash, reacts thus:—

$$S^{CSOC_2H_5}_{CSOC_2H_5} + 2KHO = CS^{OC_2H_5}_{SK} + CO^{OC_2H_5}_{SK} + H_2O.$$

With alcoholic ammonia it yields xanthamide:—

$$S^{CSOC_2H_5}_{CSOC_2H_5} + 3NH_3 = 2CS^{OC_2H_5}_{NH_2} + NH_5S.$$

Equivalent quantities of ethylene bromide and potassium xanthate react upon each other to form potassium bromide and a substance which crystallises from ether in fine highly refractive crystals melting at 42°, and having the composition indicated by the formula, $C_2H_4\left\langle\begin{matrix}S—CSOC_2H_5\\S—CSOC_2H_5\end{matrix}\right.$ (*ethylene xanthate*).

This substance is decomposed by alcoholic potash, yielding potassium xanthate, ethylene oxide, and water:—

$$C_2H_4{}^{SCSOC_2H_5}_{SCSOC_2H_5} + 2KHO = 2CS^{OC_2H_5}_{SK} + C_2H_2O + H_2O.$$

By decomposition with alcoholic ammonia it yields xanthamide and ethylene mercaptan:

$$C_2H_4{}^{SCSOC_2H_5}_{SCSOC_2H_5} + 2NH_3 = 2CS^{OC_2H_5}_{NH_2} + C_2H_4(SH)_2.$$

J. R.

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## Thiolactic Acid. By C. BÖTTINGER (Deut. Chem. Ges. Ber., ix, 1061—1064).

IN former papers the author described two sulphuretted compounds derived from pyroracemic acid, one of which agreed approximately with the formula, $C_3H_4SO_2$, whilst the other agreed with the formula, $C_3H_4SO_2 + C_3H_4O_3$ (see this Journal, 1876, ii, 70).

The former of these compounds has been found, on further examination, to have the composition required by the formula, $C_3H_6SO_2$, which is that of thiolactic acid. It crystallises from water in rectangular transparent tables, which melt at 141°. A solution of the acid neutra-

lised with ammonia gives precipitates with lead acetate and mercuric chloride. When oxidised with chromic acid it yields acetic acid, sulphur being deposited and carbon dioxide set free. The constitution of the acid is expressed by the formula, $CH_3$—CHSH—COOH.

The substance $C_3H_4SO_2 + C_3H_4O_3$, when treated with hydriodic acid, likewise yields thiolactic acid.

J. R.

## Glycocine Derivatives. By K. Kraut (Liebig's Annalen, clxxxii, 172).

When glycocine (amidacetic acid) is heated with ethyl iodide, hydriodide of ethylic amidacetate, $HI,NH_2.CH_2.CO.OC_2H_5$, is formed but no ethylated glycocine; if, however, silver glycocine (silver amidacetate) is employed, the following reaction takes place, *ethiodide of ethylic diethamidacetate* being formed, and two-thirds of the glycocine being regenerated.

$$3(NH_2.CH_2.CO.OAg) + 4C_2H_5I = C_2H_5I.N(C_2H_5)_2.CH_2.CO.OC_2H_5 + 3AgI + 2(NH_2.CH_2.CO.OH).$$

To prepare silver-glycocine, freshly precipitated silver hydrate is treated with slightly more than the theoretical amount of glycocine in warm aqueous solution, and the whole stirred till cold; the greyish crystalline powder thus produced contains, after washing and drying over sulphuric acid and finally at 100°, 60—61 per cent. of silver, the pure compound containing 59·32 per cent.: but little silver oxide is, therefore, mixed with it. On mixing this with at least 2 molecules of ethyl iodide, a slight evolution of heat ensues, and on standing for several days in the cold the whole solidifies: the solid mass is powdered and exposed to dry air to allow the excess of ethyl iodide to escape: in this state it yields only minute amounts of matter to ether; but on successive treatments with cold alcohol, cold water, and boiling baryta or caustic potash-solution, the organic products of the reaction are dissolved out. The aqueous solution contains the regenerated glycocine; the alcoholic solution contains the ethiodide of ethylic diethamidacetate: this can be transformed into ethylo-chloride by means of silver chloride, and finally into platinum ethylchloride $(C_2H_5Cl.N(C_2H_5)_2.CH_2.CO.OC_2H_5)_2PtCl_4$, crystallising in roseate monoclinic prisms of considerable size; a portion of the ethiodide remains in the silver iodide left undissolved by the alcohol and the water, and is dissolved out by the boiling alkali.

When silver-glycocine is left in contact with ethyl iodide not in excess, and the mass finally distilled, *ethylic diethamidacetate*, $N(C_2H_5)_2.CH_2.CO.OC_2H_5$ is formed; this is a colourless liquid, having an alkaline reaction, soluble in water but not in all proportions, and not solidifying at $-10°$; it boils at 177° (corrected), and has the spec. grav. 0·919 at 15°; it forms a platinum salt precipitated from alcoholic solution by ether as an oil, becoming crystalline on standing in contact with the mother-liquor; with ethyl iodide at 100° it unites forming the above-described ethiodide.

The author regards this diethamidacetate of ethyl not as directly formed from the materials used, but as probably a product of the action of the heat used to distil off the body on the mixture of ethiodide of ethylic diethamidacetate formed first, and the excess of silver glycocine, thus:—

$$C_2H_5I.N(C_2H_5)_2.CH_2.CO.OC_2H_5 + NH_2.CH_2.CO.OAg = AgI + NH_2.CH_2.CO.OC_2H_5 + N(C_2H_5)_2.CH_2.CO.OC_2H_5;$$

otherwise it is difficult to understand how the body comes to be free in the product of the reaction.

If methyl iodide be made to act on silver glycocine, the *methiodide of methylic dimethylamidacetate* is formed, from which *oxyneurine* can be produced. This reaction is being investigated.

C. R. A. W.

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## Ethylsuccinimide and Methylsuccinimide.

By N. MENSCHUTKIN (Liebig's Annalen, clxxxii, 90—93).

ETHYLSUCCINIMIDE, $C_4H_4O_2(C_2H_5)N$, is formed by distilling acid ethylamine succinate, or a solution of its constituents in the requisite proportions, and fractionating that portion of the distillate which boils between 225° and 240°. It melts at 26° and boils at 234°. Its vapour-density was found to be 4·61, air being 1 (theory requires 4·41).

Ethylsuccinimide is easily soluble in water, alcohol, and ether. In chemical properties it closely resembles succinimide. Potash resolves it completely into ethylamine and succinic acid. When gently heated with baryta-water it is converted into barium ethylsuccinamate, $[C_4H_4O_2(C_2H_5.HN)O_2]_2Ba$, which forms indistinct crystals, easily soluble in water.

*Methylsuccinimide*, $C_4H_4O_2(CH_3)N$, resembles the ethyl-compound, and is obtained in the same manner. It melts at 66·5° and boils at 234°. It crystallises from alcohol in broad laminæ, which are easily soluble also in water.

*A double-salt of mercuric succinimide and mercuric cyanide*, $(C_4H_4O_2N)_2Hg.Hg(CN)_2$, is formed on mixing hot concentrated solutions of the two constituents: it crystallises in laminæ as the liquid cools.

J. R.

## Tartronamic Acid. By N. MENSCHUTKIN (Liebig's Annalen, clxxxii, 82—90).

THIS acid is one of the products of the decomposition of sodium dialurate in presence of water. It is obtained by boiling moist freshly prepared sodium dialurate with water, until the liquid, when cold, ceases to reduce silver nitrate, and then adding a quantity of sulphuric acid exactly equivalent to the sodium present. Tartronamic acid separates at once in prismatic crystals or needles. After drying over sulphuric acid its composition agrees with the formula, $C_3H_5NO_4$. The

acid dissolves sparingly in cold water, and also in alcohol and ether. It melts at about 160°, with decomposition. It is a monobasic acid, and forms salts which crystallise very readily.

The *silver salt*, $C_3H_4AgNO_4$, obtained by precipitation or by dissolving silver oxide in the aqueous acid, dissolves in hot water and crystallises therefrom in small prisms or needles.

The *lead salt*, $(C_3H_4NO_4)_2Pb + \frac{1}{2}H_2O$, formed by saturating the acid with lead hydrate, crystallises in silky needles, which are easily soluble in hot water.

The *barium salt*, $(C_3H_4NO_4)_2Ba + H_2O$, is very soluble in water, and forms indistinct crystals.

The *potassium salt*, $C_3H_4KNO_4 + H_2O$, forms fine prismatic crystals.

Tartronamic acid is slowly decomposed by water at 100°, carbon dioxide being evolved and glycollic acid formed. Nitrous acid in presence of nitric acid resolves it into glycollic acid, carbon dioxide, and nitrogen. Its constitutional formula is—

$$CH(HO)\begin{cases} CO.NH_2 \\ CO_2H \end{cases}.$$

J. R.

## On the Composition of Dialurates. By N. MENSCHUTKIN (Liebig's Annalen, clxxxii, 70—82).

THE author's investigation has shown that Liebig and Wöhler's ammonium dialurate, $C_4H_3(NH_4)N_2O_4$, and Strecker's potassium dialurate, $C_4H_3KN_2O_4$, are derived from salts of another series, having, according to analysis, the general formula, $C_7H_8M_2N_4O_{10}$ (M being univalent). Of this latter series the ammonium, potassium, sodium, and barium salts have been examined, but their molecular constitution is not yet made out. Both series of salts are provisionally called dialurates.

*Ammonium dialurate* forms the starting-point for the preparation of other dialurates. The author prepares it either by Liebig and Wöhler's process (by the action of nitric acid on uric acid and subsequent reduction of the product by ammonium sulphide), or by Strecker's process (action of ammonia on alloxan in presence of hydrocyanic acid). The salt crystallises in long needles, agreeing approximately in composition with the formula, $C_7H_8(NH_4)_2N_4O_{10}$. It is very unstable, and when crystallised repeatedly from hot water in presence of ammonium carbonate, it is gradually transformed into microscopic prisms, which are perfectly constant in composition, and agree with Liebig and Wöhler's formula, $C_4H_3(NH_4)N_2O_4$. The latter salt acquires a rose-red colour in the air. It dissolves sparingly in boiling water, being immediately transformed into the salt $C_7H_8(NH_4)_2N_4O_{10}$. The solution gives by double decomposition salts of the same series.

*Potassium dialurate*, $C_7H_8K_2N_4O_{10}$, is obtained by mixing boiling saturated solutions of the ammonium salt and potassium acetate. It crystallises in small needles, which turn rose-red in the air. It dissolves very sparingly in boiling water, and is completely decomposed on prolonged boiling therewith. By crystallisation in presence of

much potassium carbonate it is transformed into a granular precipitate having the formula $C_4H_3KN_2O_4$, and identical with Strecker's salt. The latter, when dissolved in boiling water, is immediately reconverted into the salt $C_7H_8K_2N_4O_{10}$, in this respect resembling the ammonium salt.

*Sodium dialurate*, $C_7H_8Na_2N_4O_{10}$, is obtained in the same way as the potassium salt. It crystallises in brilliant white needles, which dissolve sparingly in boiling water, and are completely decomposed on prolonged boiling. The salt loses half a molecule of water at 130°, in accordance with the equation—

$$2C_7H_8Na_2N_4O_{10} - H_2O = C_{14}H_{14}Na_4N_8O_{19}.$$

All attempts to transform it into the salt $C_4H_3NaN_2O_4$, failed entirely.

*Barium dialurate*, $C_7H_8BaN_4O_{10}$, like the sodium salt, exists in one form only. It is obtained as a white crystalline precipitate by adding barium chloride to a dialurate of either series. It is nearly insoluble in water.

J. R.

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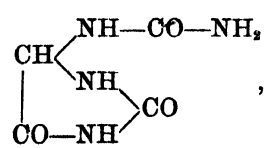
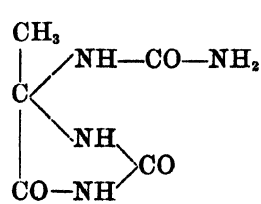
## Synthesis of Allantoïn. By Ed. Grimaux (Compt. rend., lxxxiii, 62—65).

When 1 part of glyoxylic acid is heated to 100° with 2 parts of urea for eight or ten hours, and the resulting mass, after exhaustion with alcohol, is dissolved in boiling water, the solution on cooling deposits large brilliant crystals, agreeing in composition with the formula, $C_4H_6N_4O_3$, and having all the properties of allantoïn.

Allantoïn may be represented by the constitutional formula—



which is analogous to that of pyruvil, the diureide of pyruvic acid,



and the same analogy may be traced in the derivatives of these bodies. Thus—

| $C_4H_6N_4O_3$. | $C_5H_8N_4O_3$. |
|---|---|
| Allantoïn. | Pyruvil. |

| | |
|---|---|
| $C_3H_2N_2O_2.H_2O$. Glyoxyl-urea. (Allanturic acid of Pelouze.) | $C_4H_4N_4O_2$. Pyruvil-urea. |
| $C_7H_8N_6O_5.H_2O$. Diglyoxylic triureide. (Allanturic acid of Mulder.) | $C_9H_{10}N_6O_3$. Dipyruvic triureide. |
| $C_3H_4N_2O_3$ Hydantoïn. | $C_4H_6N_2O_2$. Lactyl-urea. |

The allanturic acid of Pelouze was obtained by the action of hydrochloric acid on allantoïn, by which reaction Mulder's allanturic acid was also formed. Similarly, pyruvil yields with strong hydrochloric acid the monureide of pyruvic acid, and with dilute hydrochloric acid the triureide of the same acid.

J. R.

## On the Ammonium Compounds. By W. Lossen (Liebig's Annalen, clxxxi, 364—383).

For the purpose of ascertaining whether they were identical, or only isomerides, Victor Meyer and Lecco (*ibid.*, clxxx, 173) made a careful examination of the two dimethyldiethylammonium iodides, obtained respectively by the action of ethyl iodide on dimethylamine, and of methyl iodide on diethylamine. From the similarity in the properties of the substances obtained in these two ways, Meyer and Lecco concluded that the two bodies were identical, and not isomerides. Instead, therefore, of being molecular compounds with the formulæ, $N(CH_3)_2C_2H_5.C_2H_5I$, and $N(C_2H_5)_2CH_3.CH_3I$ respectively, they must, if identical, be regarded as the atomic compound, $NC_2H_3)_2(CH_3)_2I$, with the result of making nitrogen in the first case a triad, and in the second a pentad. It is urged, however, by the author, that Meyer and Lecco's experiments do not establish these points: for it is possible that the reaction between the dimethylamine and the ethyl iodide may not be a direct combination, but that first ethyldimethylamine may be formed by the direct action of the ethyl iodide, that this may be converted into diethylmethylamine, together with methyl iodide, by the further action of the iodide, and thence diethyldimethylammonium iodide, $N.(C_2H_3)_2CH_3.CH_3I$, may be formed. Meyer and Lecco have endeavoured to remove this objection by showing that methyl iodide is without action on tetraethylammonium; this, however, is not conclusive, the conditions being different.

It is also urged that even if the properties of the two substances obtained by Meyer and Lecco in this manner were identical, it would not prove that the two substances were not metameric, for the two dimethyldiethylammonium iodides, $N.(C_2H_5)_2CH_3.CH_3I$, and $N(CH_3)_2C_2H_5.C_2H_5I$ might possess very similar properties, from their symmetrical constitution, and it is shown that such would probably be the case. Thus tetramethylammonium chloroplatinate and trimethylethylamine chloroplatinate bear a close resemblance to each other, and have the same crystallographic structure. A similar

fact holds with tetraethylammonium chloroplatinate and triethylmethylamine chloroplatinate. The same circumstance is also found with the corresponding picrates, which form long, golden-yellow glittering needles, scarcely to be distinguished from one another, and the crystallographic constitution of the tetramethylammonium and the trimethylethylamine picrates and the tetraethylammonium and the triethylmethylamine picrates are shown to be very similar. From this great resemblance in the crystallographic constitution of the picrates and chloroplatinates of the different methyl and ethyl ammonium bases, no conclusions of weight can, it is urged, be drawn as to their identity, from the resemblance in appearance and crystalline form of the chloroplatinates and picrates of the dimethyldiethylammonium bases formed and examined by Meyer and Lecco. It is also shown that much weight must not be attached to the similarity in melting point of the two products as establishing their identity, for closely isomeric substances have often the same melting point. Moreover the steady decrease in the melting points of the picrates of the different ammonium bases affords evidence that the two isomeric diethyldimethylammonium bases would possess similar melting points. The same conclusion likewise holds with regard to the solubility of the salts of the two bases in water.

Hofmann has already shown that when an alcoholic ammonium hydrate containing ethyl is distilled, it loses ethyl, and ethylene and a triamine are formed. This is confirmed by the behaviour of trimethylethylammonium hydrate and triethylmethylammonium hydrates, which give ethylene and trimethylamine and dimethylethylamine respectively. The chlorides of the above bases behave differently, triethylmethylammonium chloride yielding a mixture of ethyl and methyl chlorides, together with triethylamine and diethylmethylamine. Diethyldimethylammonium chloride gives methyl chloride nearly free from ethyl chloride, and principally diethylmethylamine. Ethyltrimethylammonium chloride gives methyl chloride and dimethylethylamine. These last reactions would therefore appear to show that these ammonium bases are truly atomic, and not molecular compounds, as this last view presents some difficulties in explaining their distillation-products.

E. N.

## An Ethyl-derivative of Pyrrol. By C. A. Bell (Deut. Chem. Ges. Ber., ix, 935—937).

Mucic acid dissolves rapidly in a solution of ethylamine, with considerable rise of temperature. The solution, when evaporated, deposits rhombic prisms of neutral ethylammonium mucate, $C_6H_{10}O_8(C_2H_5.H_2N)_2$, which closely resemble those of the ammonium salt, but are distinguished therefrom by their great solubility in alcohol. The salt decomposes when distilled, evolving carbon dioxide. The distillate separates into two layers, the lower of which consists of a solution of ethylammonium carbonate, and the upper of *ethylpyrrol*, $C_4H_4(C_2H_5)N$. The latter liquid boils at 131°, and has the smell and external characters of ordinary pyrrol. Its sp. gr. at 16° is 0·8881.

J. R.

**On Substitution in Benzene.** By F. BEILSTEIN and A. KURBATOW (Liebig's Annalen, clxxxii, 94—112).

IN a former paper the authors stated that in the chlorination of benzene there is formed, together with solid paradichlorobenzene, a small quantity of a liquid isomeric product. The latter they have found on further investigation to be identical with the orthodichlorobenzene previously obtained by them. It was, moreover, found to differ essentially from metadichlorobenzene, which is also liquid. *Orthodichlorobenzene* boils at 179°, and yields by the action of nitric acid a substitution-product, which melts at 43°; whilst *metadichlorobenzene* boils at 172°, and yields a nitro-derivative melting at 33°. Further differences between the two substances were observed in the composition and characters of the lead and barium salts of their sulphonic acids.

ISOMERIC CHLORONITRANILINES.—*Nitroparachloraniline.*—This body was obtained by adding parachloracetanilide to concentrated nitric acid, and boiling the resulting chloronitracetanilide with potash. The same product was formed on heating nitroparadichlorobenzene (melting at 55°), with alcoholic ammonia. It forms orange-red needles, easily soluble in alcohol, ether, and acetic acid. It melts at 115°. When treated with nitrous acid and alcohol it yields metachloronitrobenzene, melting at 46°, and boiling at 233°. The latter substance, by reduction with tin and hydrochloric acid, yields liquid metachloraniline. Hence the substance obtained as above is *ortho*nitroparachloraniline, $C_6H_3(\underset{1}{NH_2})\underset{4}{Cl}(\underset{2}{NO_2})$.

*Nitro-orthochloranilines.*—Orthochloracetanilide yields by treatment with strong nitric acid, and subsequent distillation of the product with soda, the two following bodies:—

1. *Metanitro-orthochloraniline.*—Yellow needles, melting at 117—118°, and very easily soluble in alcohol, ether, acetic acid, and acetone. It yields with acetyl chloride an acetyl-derivative, which crystallises in needles melting at 153—154°. By treatment with nitrous acid and alcohol it is converted into parachloronitrobenzene, melting at 83°, and yielding by reduction solid parachloraniline. The constitution of the body is therefore expressed by the formula, $C_6H_3(\underset{1}{NH_2})\underset{2}{Cl}(\underset{5}{NO_2})$.

2. *Paranitro-orthochloraniline.*—This substance is formed in small quantity only. When treated with nitrous acid and alcohol, it yields metachloronitrobenzene, which melts at 46°, and yields by reduction metachloraniline. Hence its formula is $C_6H_3(\underset{1}{NH_2})\underset{2}{Cl}(\underset{4}{NO_2})$.

*Nitrometachloranilines.*—Metachloracetanilide, when treated in the same manner as the ortho-anilide, likewise yields two nitrochloranilines:—

1. *Orthonitrometachloraniline* crystallises from carbon bisulphide in golden-yellow needles. It dissolves easily in alcohol, ether, and acetic acid, and melts at 124—125°. With acetyl chloride it yields an acetyl derivative, which crystallises in needles melting at 115°. By treatment with nitrous acid it gives solid parachloronitrobenzene, which melts at 83°, and yields by reduction parachloraniline, melting at 70—71°. Its formula is, therefore, $C_6H_3(\underset{1}{NH_2})\underset{3}{Cl}(\underset{6}{NO_2})$.

2. *Paranitrometachloraniline* crystallises from benzene in yellow laminæ, melting at 156—157°, and dissolving easily in alcohol and acetic acid. It forms with acetyl chloride an acetyl derivative, which crystallises in pale-yellow needles, melting at 141—142°. When treated with nitrous acid and alcohol it is converted into a chloronitrobenzene, which crystallises in needles melting at 32·5° and boiling at 243°. The latter substance yields, by reduction with tin and hydrochloric acid, liquid orthochloraniline, together with some dichloraniline. These reactions show that the formula of this nitro-derivative is $C_6H_3(\underset{1}{NH_2})\underset{3}{Cl}(\underset{4}{NO_2})$.

CHLORONITRANILINES FROM DICHLOROBENZENES.—1. Nitroparadichlorobenzene, when heated with ammonia, yields *orthonitroparachloraniline*, melting at 115° (see above).

2. Nitro-orthodichlorobenzene (melting at 43°), when heated with alcoholic ammonia, yields *paranitro-orthochloraniline*. This substance forms yellow needles, melting at 104—105°, and dissolving easily in alcohol, ether, and carbon bisulphide. It yields an acetyl derivative, crystallising in colourless needles, which melt at 139°.

3. Nitrometadichlorobenzene (melting at 33°), when heated with alcoholic ammonia, yields *orthonitrometachloraniline*, melting at 124—125°, as described above.

J. R.

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## Action of Chloroform on Alkaline Phenolates. By K. REIMER and F. TIEMANN (Deut. Chem. Ges. Ber., ix, 824—828).

THE authors have previously shown that salicylic aldehyde is formed when chloroform is made to act upon a strongly alkaline solution of phenol, in accordance with the equation—

$$C_6H_5.ONa + 3NaOH + CHCl_3 = 2H_2O + 3NaCl + C_7H_5O_2Na.$$

They now find that the yield of salicylic aldehyde is always far below the theoretical amount, and have traced the loss to at least two different reactions of another kind. In the first place, besides salicylic aldehyde, the isomeric *paroxybenzoic aldehyde* is formed; and secondly, a resinous red product is formed, which appears to be, as Guareschi pointed out some years ago, either identical with, or closely allied to, the *rosolic acid* obtainable from phenol and oxalic acid by the process of Kolbe and Schmitt. Admitting that this body is expressed by the formula, $C_{20}H_{14}O_3$ (as is most probable from the researches of Dale and Schlormmer), it is readily conceivable that it may be formed by the action of phenol on salicylic aldehyde, under the dehydrating influence of the excess of alkali present. Thus:—

$$2C_7H_6O_2 + C_6H_6O = C_{20}H_{14}O_3 + 2H_2O.$$

Indeed, the rosolic acid produced by the agency of oxalic acid is very probably formed by this same mechanism; for Fresenius has shown that formic acid may be substituted for oxalic acid, which thus appears to act by breaking up into carbon dioxide and formic acid, which latter, whilst nascent, converts the phenol into salicylic aldehyde, with elimi-

nation of water, the nascent salicylic aldehyde then forming rosolic acid, as above. Liebermann has subsequently succeeded in obtaining from salicylic aldehyde and phenol crystallised rosolic acid, apparently identical with that from oxalic acid.

In order to obtain salicylic and paroxybenzoic aldehydes, the following process may be used:—15 parts of chloroform are gradually introduced by vigorous shaking into a warm (50°—60°) solution of 10 parts of phenol and 20 of sodium hydrate in 30—35 of water; an action speedily commences, the slightly yellow liquid soon becoming blue or reddish-violet, and finally deep red; the temperature rises, so that to avoid loss of chloroform it is necessary to affix a reflux condenser. After half an hour's boiling the small quantity of chloroform that remains unacted on is distilled off, and hydrochloric or diluted sulphuric acid is cautiously added to the residue, until a strong acid reaction is manifest; a thick dark red oil, smelling strongly of salicylic aldehyde, is thus precipitated. On blowing steam through the whole, salicylic aldehyde and phenol pass over along with the water vapour, whilst a red resinous mass and a slightly yellow aqueous liquor remain in the distilling flask; this latter solution is filtered off through a wet filter, and, after cooling, well agitated with ether, which takes up a body crystallising on evaporation in stellate needles, more or less yellow coloured. This substance is readily soluble in cold water, and even more so in hot water, alcohol, and ether; from an ethereal solution it is completely removed by agitation with aqueous sodium hydrogen sulphite, no difficultly soluble compound being, however, produced. After crystallisation from boiling water, this body forms white needles, melting at 115°—116°; its aqueous solution gives a faint violet coloration with ferric chloride. On analysis it gives numbers agreeing with $C_7H_6O_2$; and as oxidising agents (notably fusion with caustic potash) convert it readily in paroxybenzoic acid, it is manifest *paroxybenzoic aldehyde*. Bücking obtained a short time ago from anisic aldehyde a body possessed of the same properties as this substance, but melting a few degrees lower.

In order to separate pure salicylic aldehyde from the distillate obtained as above, the distillate is shaken with ether, and the ethereal extract with sodium hydrogen sulphite, whereby the phenol present is readily separated.

It hence appears that just as carbonic acid and alkaline phenolates give rise to *two* isomeric carboxylated phenols (salicylic and paroxybenzoic acid), so nascent formic acid (from the action of alkalies on chloroform) gives rise under the same conditions to two isomeric aldehydes, similarly related to the parent phenol, viz., salicylic and paroxybenzoic aldehydes. The authors, however, have not been able to trace out any difference in the result, according as potash or soda is used in the chloroform process, whilst this difference is very marked with the carbonic acid reaction. The relative quantities of the two isomeric aldylated* phenols formed depend much more on the tem-

* *Note by Abstractor.*—The term "aldyl" may be conveniently used to designate the radical COH, characteristic of the aldehyde family; so that parabenzoic aldehyde may be conveniently termed *paraldyl-phenol*, just as paroxybenzoic acid is known as *paracarboxyl-phenol*.—C. R. A. W.

perature and concentration of the liquid employed, than on the nature of the alkali present.

C. R. A. W.

## Xylenol from Metaxylene. By S. LAKO (Liebig's Annalen, clxxxii, 30—33).

THE only researches on xylenol hitherto published are those of Wurtz and Wroblevsky, who obtained it by fusing with potash the potassium salt of xylenesulphonic acid. The crude xylene employed by these chemists having since been shown by Fittig to be a mixture of two isomeric dimethylbenzenes, the author has now repeated Wurtz's experiments with pure metaxylene or isoxylene. This substance was obtained by heating crude xylene with dilute nitric acid (1 to 3) till nitrated products ceased to be formed. It yields a sulphonic acid, the barium salt of which is moderately, and the potassium, magnesium, and sodium salts very easily soluble. The xylenol obtained by fusing the potassium salt with potash is an oily liquid, highly refractive, boiling at 206·5—208·5°, smelling distinctly of phenol, and agreeing in composition with the formula $C_8H_{10}O$. Its vapour-density was found to be 58·4, and its sp. gr. 1·0366 at 0°, and 1·0242 at 15·5°. It yields a nitro-derivative $C_6H_2(CH_3)_2(NO_2)HO$, which melts at 68·5°, crystallises in yellow needles, and forms a potassium salt crystallising in dark-red laminæ.

J. R.

## On the various Hydrobenzoïns or Stilbene Alcohols. By C. FORST and TH. ZINCKE (Liebig's Annalen, clxxxii, 241—295).

HITHERTO no fewer than four bodies of the formula $C_{14}H_{14}O_2$ have been described by different chemists:—(1.) Zinin's hydrobenzoïn, obtained by the action of zinc and alcoholic hydrochloric acid on bitter almond oil: (2.) Church's dicresol, obtained by the action of sodium alcohol on the same substance: (3.) Limpricht and Schwanert's toluylene alcohol, obtained from stilbene bromide: and (4.) Fittig and Ammann's hydrobenzoïn, formed by the action of sodium amalgam on bitter almond oil in presence of water. The authors of the present paper, having repeated the processes by which these various bodies are said to have been formed, have arrived at the conclusion that bitter almond oil, benzoïn, and stilbene, yield by known methods only *two* alcohols, namely, the *hydrobenzoïn* of Zinin, and the *isohydrobenzoïn* of Fittig and Ammann. Bitter almond oil yields both these products simultaneously; benzoïn yields only hydrobenzoïn; whilst stilbene bromide yields one or the other according to circumstances. The so-called dicresol and toluylene alcohol are regarded as mixtures of hydrobenzoïn and isohydrobenzoïn.

*Hydrobenzoïns (Stilbene Alcohols) from Bitter Almond Oil.*—These substances were obtained by the authors (1) by the action of sodium amalgam on bitter almond oil in presence of water (the best proportion being 1 of oil to 4 of water); (2) by the action of sodium amalgam on an ethereal solution of the oil; (3) by the action of the amalgam

on the oil in presence of acetic acid. In all cases the product was a mixture of hydrobenzoin and isohydrobenzoïn, no other well-characterised substance being formed.

*Hydrobenzoïn from Benzoïn and Benzile.*—Benzoïn treated with sodium amalgam in presence of alcohol or water yields hydrobenzoïn but no isohydrobenzoïn, some benzoic acid being formed at the same time.

Benzile, when heated with sodium amalgam and water, yields a large quantity of hydrobenzoïn, together with a small quantity of a body crystallising in needles which melt at 60°.

*Hydrobenzoïns from Stilbene Bromide.*—Stilbene bromide, when heated with *silver acetate* and glacial acetic acid, yields the diacetates of hydrobenzoïn and isohydrobenzoïn, and monacetate of isohydrobenzoïn. These three products are separable by fractional precipitation with water: by saponification with alcoholic potash they yield hydrobenzoïn and isohydrobenzoïn, the former preponderating.

Stilbene bromide, heated to 160° with *potassium acetate* and glacial acetic acid, yields isohydrobenzoïn diacetate and monacetate, but no hydrobenzoïn acetate. When alcohol is substituted for glacial acetic acid, the product is a mixture of stilbene and monobromostilbene.

Stilbene bromide, heated with *silver benzoate* in xylene, yields hydrobenzoïn and isohydrobenzoïn dibenzoates, the former preponderating.

Stilbene bromide, treated with *silver oxalate* in xylene, yields a large quantity of stilbene, and a number of resinous products, which by saponification with alcoholic ammonia give almost exclusively hydrobenzoïn.

*Hydrobenzoïn*, $C_{14}H_{12}(OH)_2$, as obtained by the authors, melts at 134° and crystallises from hot acetic acid or weak spirit in fine glittering laminæ, and from hot absolute alcohol in large, thin, transparent, rhombohedric tables, which latter are obtained also by slow evaporation of its solution in benzene, benzoline, or chloroform.

The *monacetate*, $C_{14}H_{12}(OC_2H_3O)(OH)$, formed together with the diacetate by heating hydrobenzoïn to 170° with glacial acetic acid, forms long pointed needles, which melt at 84°, and dissolve easily in alcohol, ether, and acetic acid.

The *diacetate*, $C_{14}H_{12}(OC_2H_3O)_2$, formed as described above, and also by the action of acetic anhydride or acetyl chloride on stilbene bromide is soluble in hot alcohol, from which it crystallises in large colourless prisms melting at 134°. It dissolves also in ether, benzene, and chloroform.

The *monobenzoate*, $C_{14}H_{12}(OC_7H_5O)(OH)$, is formed, together with the dibenzoate, by heating hydrobenzoïn to 150—160° with benzoic anhydride. It forms fine brilliant needles or laminæ, which melt at 160—161°, and dissolve easily in hot alcohol, ether, and chloroform.

The *dibenzoate*, $C_{14}H_{12}(OC_7H_5O)_2$, formed as above, or by the action of benzoyl chloride on hydrobenzoïn, is characterised by its very sparing solubility. It dissolves only slightly in cold ether, alcohol, chloroform, and benzene, and rather more freely in boiling acetic acid, xylene. and hot alcohol, from which solvents it crystallises in small shining brittle needles, melting without decomposition at 247°.

*Isohydrobenzoïn* dissolves easily in alcohol, ether, and chloroform, and is deposited therefrom in well-formed crystals. It crystallises

from hot water either with or without water of crystallisation according to circumstances. The hydrated crystals are clear and colourless, and melt at 95—96°, but they quickly lose water and become opaque. The anhydrous crystals, which are monoclinic, melt at 119—120°.

The *monacetate*, formed by the action of potassium or silver acetate on stilbene bromide, resembles the isomeric hydrobenzoïn-compound in its behaviour with solvents, but crystallises in thicker, shorter needles, and melts at 87—88°.

The *diacetate* is likewise formed, though only in small quantity, by the action of potassium or silver acetate on stilbene bromide. It is most easily obtained by heating the monacetate with acetic anhydride, or by treating it with acetyl chloride, but by the latter reaction some chlorinated products are formed at the same time. Its hot alcoholic solution deposits shining laminæ, resembling stilbene, and melting at 117°, whilst the mother-liquor of these laminæ yields, on spontaneous evaporation, fine brilliant prisms, which melt when first heated at 117—118°, but afterwards at 105—106°. A solution in cold alcohol of the laminæ melting at 117—118°, when evaporated slowly, yields prisms melting when first heated at 117—118°, and afterwards at 105—106°. Both crystalline forms are easily soluble in alcohol, ether, and chloroform.

The *monobenzoate* is obtained, though only in very small quantity, by the same reaction as the corresponding hydrobenzoïn-compound; it is also formed in small quantity when isohydrobenzoïn is heated to 150—160° with excess of benzoic anhydride, in which reaction the dibenzoate and *hydrobenzoïn* dibenzoate are also formed, so that there is in the reaction a direct transformation of isohydrobenzoïn into its isomeride. It crystallises from weak spirit in small shining needles, which melt at 130°, and dissolve in ether and chloroform.

The *dibenzoate* is formed, together with the corresponding hydrobenzoïn-compound, by the action of silver benzoate on stilbene bromide, or by the action of benzoic anhydride on isohydrobenzoïn. It forms colourless needles or laminæ, melting at 155—166°, and dissolving in hot alcohol, ether, and chloroform.

The foregoing results establish beyond doubt the identity of the alcohols obtained from stilbene bromide with hydrobenzoïn and isohydrobenzoïn from bitter almond oil; and the number of alcohols of the formula $C_{14}H_{12}(OH)_2$ is thus reduced to two. Of the constitution of these bodies, and the ground of their isomerism, nothing is yet definitely known.

J. R.

## Anthraflavone. By A. Rosenstiehl

(Compt. rend. lxxxii, 1394—1396.)

In this paper the author gives a summary of his own experiments on this substance. When it is fused with potash, two colouring matters are produced: one, soluble in benzene and in alum-water, gives tints like those of alizarin; the other, insoluble in these liquids, resembles purpurin. The former has not been obtained in quantities sufficient for examination: the latter is an isomeride of purpurin, and its pro-

perties approach those of the isopurpurin or anthrapurpurin of Perkin. Anthraflavone is a mixture of two isomerides of alizarin; one of which forms a very soluble soda-salt, gives an orange-lake with alumina, and by fusion with caustic potash yields the isomeride of purpurin above referred to. The other forms a sparingly soluble soda-salt, does not unite with gelatinous alumina, and gives no colouring matter when fused with potash, or, at least, only at a temperature at which it is partially decomposed. This second substance is an accessory product in the manufacture of artificial alizarin, and the author has obtained samples of it from a manufactory at Prague; he believes it to be identical with the body which Schunck and Rœmer have described under the names of anthraflavic and isoanthraflavic acid.

R. R.

## Quino-acetate of Calcium. By E. Gundelach (Compt. rend. lxxxii, 1268).

In examining a commercial quinate of calcium, it was found that it was essentially a double salt, composed of equal numbers of molecules of quinate and acetate of calcium. This salt may be artificially formed by mixing together the constituents in the proper proportions, *i.e.*, 12·04 grams of quinate, and 3·52 grams of acetate of calcium. It is a stable salt, very soluble in water, but almost insoluble in absolute alcohol. It contains one molecule of water, which is not driven off by prolonged heating at 150°; above this temperature it disengages acid vapours, and carbonises at about 200°.

J. W.

## Action of Aniline on Chloral and on Chloral Hydrate. By D. Amato (Gazzetta chimica italiana, v, 461—467).

When chloral is gradually added to pure aniline in the proportion of one molecule of the former to two of the latter, an action takes place accompanied by elevation of temperature, and the dense liquid product thus obtained, after being heated to 50—60° for three or four hours, is transformed into a crystalline mass, the reaction being:

$$CCl_3CHO + 2C_6H_5NH_2 = CCl_3CH\left\{\begin{matrix} NHC_6H_5 \\ NHC_6H_5 \end{matrix}\right. + H_2O.$$

The formation of this product has been already noticed by the author in the *Gaz. chim. ital.* (1871, p. 376). The same substance is formed when chloral hydrate is employed, but in this case there is no rise of temperature, and the heating must be continued for more than nine hours. It should be observed that unless the aniline employed be pure, no trace of crystalline compound can be obtained.

The crude product may be purified by pulverising it, washing with a very small quantity of alcohol, and then recrystallising it by the spontaneous evaportaion of its solution in ether-alcohol. It is thus obtained in four-sided plates which melt at 100°, and are soluble in alcohol, ether, and benzene, but insoluble in water. It decomposes when heated, as do also its solutions. Heated with excess of calcium

or potassium hydrate, it is decomposed, ammonia being evolved and a mixture of water, aniline, and phenyl cyanide distilling over.

$$CCl_3CH\left\{\begin{matrix}NHC_6H_5\\NHC_6H_5\end{matrix}\right. 3KHO = 2C_6H_5CN + 3KCl + 3H_2O.$$

The new substance possesses basic properties, combining directly with hydrochloric acid to form two hydrochlorides of the composition $CCl_3CH\left\{\begin{matrix}NHC_6H_5\\NHC_6H_5\end{matrix}\right.HCl$ and $CCl_3CH\left\{\begin{matrix}NHC_6H_5HCl\\NHC_6H_5HCl\end{matrix}\right.$ The first of these may be prepared by passing a current of dry hydrochloric acid over the finely powdered base for a short time, but by the prolonged action of the gas it is gradually converted into the second compound, which may also be obtained in large crystals by dissolving the base in concentrated aqueous hydrochloric acid and allowing the solution to stand. If dry hydrochloric acid be passed into an ethereal solution of the base, a white crystalline powder is precipitated which is the hydrochloride with two molecules of HCl; the compound with one HCl is not formed by this process. It is necessary to dry the dihydrochloride in an atmosphere of hydrochloric acid, as it loses acid in contact with air or in a vacuum. Both the hydrochlorides crystallise in lustrous needles which are volatile even at the ordinary temperature; they are very soluble in water and in alcohol, but only very slightly soluble in ether; the alcoholic solution decomposes slowly in the cold, but more rapidly when heated. The monohydrochloride melts at 196°, the dihydrochloride appears to sublime without previous fusion.

The chloroplatinate of the base is easily obtained by adding an alcoholic solution of platinum tetrachloride to a concentrated alcoholic solution of the hydrochloride of the base, washing the precipitate rapidly with alcohol, pressing, and drying *in vacuo*. It may also be obtained by mixing the aqueous solutions, but then it is much more difficult to purify. It crystallises in lustrous gold coloured scales of the formula $\left[CCl_3CH\left\{\begin{matrix}NHC_6H_5\\NHC_6H_5\end{matrix}\right.HCl\right]_2PtCl_4$. It is very soluble in water, less so in alcohol and ether.

C. E. G.

## Phenylene-diamine. By A. Krause (Deut. Chem. Ges. Ber., ix, 835).

When phenylene diamine, melting at 140°, is heated to 190—200° for several hours with one molecule of phenylene-diamine hydrochloride, sal-ammoniac is formed, together with a blue colouring matter of which the hydrochloride is soluble in water and more so in alcohol; from the alcoholic solution microscopic crystals can be obtained.

Similarly phenylene-diamine furnishes, on treatment with aniline hydrochloride, a violet dye-stuff. The author proposes to investigate the nature of these reactions, whether ammonia is evolved and simple condensation of two molecules into one takes place, or whether the ensuing changes are of a more complex character.

C. R. A. W.

**Composition of Aniline Black.** By F. GOPPELSROEDER (Compt. rend., lxxxii, 1392—1394).

THE black was prepared by electrolysing an aqueous solution of pure aniline hydrochloride, and the deposit was purified by successive treatment with water, alcohol, and ether. The mean results of eleven analyses were: carbon 71·366; hydrogen 5·241; nitrogen 15·327; chlorine 8·941. These results would agree with the formula, $C_{24}H_{21}N_4Cl_5$, and the author regards this black as a chloride, the base of which is the tetramine, $C_{24}H_{20}N_4$, which, like other polybases of the aromatic series, readily forms monobasic salts.

R. R.

**Simple Mode of Preparing Doubly Substituted Ureas.** By W. WEITH (Deut. Chem. Ges. Ber., ix, 821).

BAEYER has prepared diphenyl urea by acting on urea with aniline; the author employs the same reaction, using, however, monophenyl urea as starting point; this body separates in crystals on mixing one molecule of aniline hydrochloride with one of potassium cyanate; and on heating the product with aniline (after thorough drying) forms almost the theoretical amounts of ammonia and *diphenyl urea*, in accordance with the reaction:

$$CO\left\{\begin{matrix}NH_2\\NH.C_6H_5\end{matrix}\right. + NH_2.C_6H_5 = CO\left\{\begin{matrix}NH.C_6H_5\\NH.C_6H_5\end{matrix}\right. + NH_3.$$

After boiling the product of the reaction with dilute hydrochloric acid to separate any urea or monophenyl urea that may be formed, and washing with warm water and finally with cold alcohol, an almost pure product is obtained; by crystallisation from alcohol prisms melting at 235° are formed; these exhibit all the properties of diphenyl urea, giving rise to carbon dioxide and aniline on heating with hydrochloric acid, and to *α-triphenyl guanidine* and carbon dioxide when heated alone to a temperature above their melting-point. By distillation with phosphoric anhydride, *phenyliso-cyanate* is readily obtained, possessing the characteristic odour, boiling at 163°, and producing monophenyl urea (melting at 144·5°) by treatment with ammonia, diphenyl-urea (melting at 235°), with aniline, and so on.

In the same way other doubly substituted aromatic ureas may be readily formed; thus monoparatolyl urea forms *diparatolyl urea* when heated with paratoluidine, the yield being 97·3 per cent. of the theoretical quantity. The resulting substance crystallises from alcohol in colourless needles resembling benzoic acid, melting uniformly at 255°; on heating them with phosphorus trichloride, considerable quantities of *triparatolyl guanidine* are formed.

C. R. A. W.

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**Reactions of Phenol with some of the Cinchona Alkaloïds.** By O. HESSE (Liebig's Annalen, clxxxii, 160—163).

WHEN equal molecular weights of cinchonidine and phenol are dissolved in dilute alcohol and mixed, an oily liquid separates and on standing

becomes crystalline; if strong alcohol be employed, fine crystals are produced, constituting colourless, glassy, odourless prisms, stable in the air, but evolving phenol on heating: these have the composition $2C_{20}H_{24}N_2O_4.C_6H_6O$, whence the author terms the compound *semi-phenol cinchonidine;* the whole of the associated phenol is expelled at 130° and is lost on repeatedly crystallising from alcohol. This substance is capable of combining with acids, *e.g.*, sulphuric acid forming the double phenolo-sulphate formerly described (this Journal, 1876, ii, 313); in alcoholic solution it has a strongly alkaline reaction, and precipitates ferric oxide from a solution of a chloride. Addition of excess of acid causes the separation of phenol, a cinchonidine salt being formed.

If 2—3 molecules of phenol are employed for one of cinchonidine, crystals are obtained containing more phenol, being represented by the formula $2C_{20}H_{24}N_2O,3C_6H_6O$; whence the author terms this body *sesqui-phenol cinchonidine.* No more phenol becomes added on recrystallisation from alcohol containing much phenol; on solution in hot alcohol, or on gently heating, the crystals are partly decomposed, with evolution of phenol; when one part of sesqui-phenol cinchonidine is dissolved in about five of alcohol, the crystals which separate have about the composition of *semi-phenol cinchonidine;* with larger quantities of alcohol a smaller amount of phenol is retained, and finally pure cinchonidine separates. On saturating the hot alcoholic solution with sulphuric acid, cinchonidine phenolo-sulphate $2C_{20}H_{24}N_2O.C_6H_6O.H_2SO_4.4H_2O$ crystallises out on cooling.

Although quinine and cinchonidine readily combine with phenol, the dextro-rotatory cinchona alkaloïds, cinchonine, quinidine, and quinamine crystallise unchanged from an alcoholic solution containing phenol, whatever may be the proportion between the alkaloid and phenol present.

C. R. A. W.

## The Constituents of Tolubalsam. By E. Busse (Deut. Chem. Ges. Ber., ix, 830).

Somewhat contradictory results have been arrived at by Fremy, Deville, Kopp, Scharling, and Carles, partly at least due to the fact that the mode of operating was calculated in some cases to bring about decomposition of the bodies originally present. The author dissolved 1 kilo. of partly resinized tolu balsam in 2 litres of ether, filtered the liquid from a little insoluble matter, and then agitated it with 2 litres of soda-solution containing 100 grams $Na_2O$; after agitating the ethereal liquor again with soda, and washing with water, a residue was obtained on distilling off the ether, consisting of 85 grams of fluid neutral compounds. On fractional distillation, a little passed over below 200°, more between 250° and 300°, and most of all above 320°. The first of these fractions appeared on analysis to be impure benzylic alcohol; it formed benzoic aldehyde and acid on oxidation. The second gave a distillate at 300°, consisting of *benzyl benzoate*, $C_{14}H_{12}O_2$; on saponification it formed benzylic alcohol and a benzoate. The third portion consisted of *benzyl cinnamate*, $C_{16}H_{14}O_2$; it furnished

cinnamic acid and benzylic alcohol on saponification, and had the spec. grav. 1·1145 at 16°.

Hence the neutral constituents of tolu balsam are the same as those found by Kraut in Peru balsam, only they exist in smaller quantity and different proportions, benzyl cinnamate forming the majority in the first, benzyl benzoate in the second.

The soda liquors obtained as above described were saturated with carbonic acid, whereby much resin was precipitated; the filtrate yielded a precipitate on addition of hydrochloric acid; one-half of the cinnamic acids thus thrown down was boiled with milk of lime; a sparingly soluble lime salt was thus obtained containing (after recrystallisation) 10·26 per cent. of calcium, the cinnamate requiring 10·30 per cent.: from this cinnamic acid melting at 133° was isolated. The mother-liquors of the sparingly soluble calcium cinnamate contained much calcium benzoate, which crystallised out after concentration: this gave (after several recrystallisations) numbers agreeing with the formula $Ca(C_7H_5O_2)_2 + 3H_2O$; and from it benzoic acid was precipitated, melting at 120·5°.

The other half of the mixture of acids was dissolved in alcohol and treated with hydrochloric acid gas; by fractional distillation the ethers thus formed were separated; the portion distilling at 215° gave numbers agreeing with the formula, $C_9H_{10}O_2$, *ethyl benzoate;* that passing over at 265° agreed with $C_{11}H_{12}O_2$, *ethyl cinnamate.*

Hence tolubalsam contains free benzoic and cinnamic acids, as well as their benzylic ethers.

C. R. A. W.

**Cynanchol.** By O. Hesse (Liebig's Annalen, clxxxii, 163).

Butleroff has recently described under this name a substance crystallising in needles and plates, derived from the sap of the *Cynanchum acutum.* The author considers this to be a mixture of *echicerin* and *echitin*, the former of which crystallises in needles, the latter in plates. In order to separate these bodies completely, large quantities must be worked with.

C. R. A. W.

**On Aloïn from Barbadoes Aloes.** By E. Schmidt (Arch. Pharm. [3], vi, 496—509).

The aloïn employed was prepared by treating aloes with dilute sulphuric acid, whereby, after the deposit of resin had been removed, aloïn was obtained in the crystalline state: this proved a better method than treatment with dilute hydrochloric acid. The crystals thus obtained were well-formed yellow needles, soluble in water and alcohol, possessing a bitter taste, but no saffron-like smell.

They can be obtained hydrous and anhydrous; in the former case melting at 70—80°, in the latter at 146—148° (Stenhouse 150°). The amount of crystallisation-water, which varies from 5·89 per cent. to 14·29 per cent., depends upon the concentration and temperature of the solution. The crystals lose water whether dried in the air or over

sulphuric acid, or heated to 100°; this may account for the fact that Stenhouse found only 2·69 per cent. of crystallisation-water, he having in all probability first dried the crystals over sulphuric acid. If allowed to stand over sulphuric acid, they can lose 13·44 per cent.

According to Tilden, the formula of aloïn is $C_{16}H_{18}O_7$; this he has determined by the aid of chlorine derivatives, but this formula the author disputes, giving $C_{15}H_{16}O_7$, he having obtained as a mean C = 59·23, H = 5·61, O = 35·16, and in another series of analyses made by Liebelt, C = 58·46, H = 5·61, O = 35·93. These numbers correspond with $C_{15}H_{16}O_7$, in which C = 58·44, H = 5·19, or to $C_{15}H_{17}O_7$, in which C = 58·25, H = 5·5, whereas $C_{16}H_{18}O_7$ requires C = 59·62, H = 5·59. Of the first two formulæ the author prefers the second, because his numbers more closely correspond with it, and also because that is the formula given by Sommaruga and Egger in their analyses of the aloïn from Soccotrina aloes. By repeated crystallisation or by careful heating aloïn undergoes a change, a brown coating being formed, probably in consequence of absorption of oxygen. Stenhouse gives $C_{17}H_{18}O_7$ as the formula of aloïn, which does not agree with the present formula when the elements of water are subtracted from it. Chlorine and bromine produce with aloïn, compounds of uncertain composition, probably because of the presence of higher and lower substitution-products than trichlor- and tribromaloïn; these products are difficult to separate, as they are soluble to nearly the same amount. The bromide crystallises with varying amounts of water. Tilden's observation that nitric acid produces with aloïn, chrysammic, picric, and oxalic acids is confirmed, with the addition, that carbonic anhydride is also formed, the quantity of this last depending on the concentration of the nitric acid, on the temperature, and on the duration of the action. Zinc dust produces principally methylanthracene and anthraquinone. Aloïn melted with potash dissolves in water with a blood-red colour; an acid may be separated from the solution, but it has not yet been examined.

E. W. P.

## Essence of Cubebs. By A. Oglialoro (Gazzetta chimica italiana, v, 467—472).

Whilst examining a specimen of essence of cubebs the author found that he obtained a hydrocarbon $C_{10}H_{16}$ boiling at 160°, which appears to have been unnoticed by any previous experimenter, although he did not succeed in separating the hydrocarbon of boiling-point 230° mentioned by Schmidt. This induced him to prepare some of the essential oil from cubebs by distilling the substance in a current of steam in a copper still; the yield was about 4 per cent., and the product, when submitted to careful rectification after being dried over calcium chloride, yielded a small quantity of a hydrocarbon, $C_{10}H_{16}$, belonging to the terpene series, boiling at 158—163°, and a considerable portion boiling at 250—270°,—evidently a mixture,—but no trace of the hydrocarbon boiling at 230° observed by Schmidt.

The portion boiling at 250—270° was mixed with half its weight of ether and saturated with hydrochloric acid; by this means a crystal-

line hydrochloride of the composition $C_{15}H_{24},HCl$, was separated, whilst the mother-liquors, after evaporation of the ether, and separation of a further portion of the hydrochloride which crystallised out, was washed with dilute alkali, dried, and submitted to fractional distillation. The greater portion passed over at 262—263°, and possessed a slight lævorotary power, although it is doubtful whether this is inherent in the hydrocarbon, or is due to the admixture of a small amount of that which forms the crystalline hydrochloride. The hydrochloride crystallises from boiling alcohol in long colourless needles, which melt at 117—118°, and when heated for some time to 170—180° with water in sealed tubes, is completely decomposed into hydrochloric acid and a hydrocarbon of the formula $C_{15}H_{24}$. This, after purification by rectification from sodium, has a density of 0·9289 at 0°, and boils at 264—265°. In a tube 10 centimeters long it deflects the polarised ray 44·50 degrees (160° 12′) to the left.* The hydrochloride also has considerable action on polarised light.

C. E. G.

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## Carvol.

By F. A. Flückiger (N. Rep. Pharm., xxv, 280—288).

After a short historical sketch, the author states that late researches on cymene leave little more than the optical properties of that hydrocarbon from different sources to be studied. Oxycymene (carvacrol) from oil of caraway, and probably from other sources, is optically inactive. Several oils have therefore been tested for carvol, advantage being taken of the property of carvol to combine with hydrogen sulphide, forming carvol hydrosulphide $(C_{10}H_{14}O)_2SH_2$, even if carvol be present together with other oils. The method employed was to dilute the oil to be tested with $\frac{1}{4}$ vol. of alcohol (0·830 sp. gr.), and then to saturate with hydrogen sulphide; the crystals obtained on addition of concentrated ammonia were washed with alcohol, and treated with alcoholic soda, pure carvol then separating on addition of hot water. Carvol prepared from caraway oil, in a tube 25 mm. long rotates to the right to the amount of 15·6°. Oil of turmeric contains no carvol, contrary to Bolley's statements, although an oil is present rotating 4·5—6° to the right, and boiling above 320°: the crystals which Bolley obtained were probably ammonium sulphide. No carvol was found in oil of myrrh, which Rinkoldt stated to be present, although an oil answering to the formula $C_{22}H_{32}O$ was obtained. Oils of the composition $C_{10}H_{14}O$ are apparently present in nutmegs and eucalyptus oils. Gladstone showed that nutmeg oil does not combine with hydrogen sulphide; this the author corroborates, as well as announcing that he has been unable to detect carvol in eucalyptus oil, or in oil of mace. Carvol from oil of dill (*Anethum graveolens*) has the same optical properties as that obtained from oil of caraway. Oil of spear-mint (not peppermint), also called menthol, contains carvol having a lævorotatory power of 7°, whereas it is absent in peppermint oil. German

* The author neither states what apparatus was used in these experiments, nor whether monochromatic light was employed, so that it is impossible to compare his results satisfactorily with those obtained by other observers.—*Abstractor.*

spear-mint oil (Krauseminzöl) yields, on saturation with hydrogen sulphide, 70 per cent., with a lævorotatory power of 7°. After separation of all crystallisable sulphide, and on further addition of ammonia and hydrogen sulphide, thiocarvol $(C_{10}H_{14}S)_2SH_2$, is obtained as a viscous oil, inodorous after purification. It is attacked by concentrated nitric acid without formation of sulphuric acid, whereas a crystallised hydrosulphide of carvol is not attacked by nitric acid. The carvol of curled mint, which differs from that of dill and caraway, rotates to the left about 9°, less therefore than that of dill oil, taken in the opposite direction (dill. 20°). When dextro- and lævo-carvol are compared, it may be found that the latter will yield an inactive oxycymene (carvacrol) and derivatives such as have been prepared from caraway oxycymene and camphor thiocymene.

E. W. P.

## Oil of Iris-root. By F. A. Flückiger (Arch. Pharm. [3], vi, 481—487).

On distillation with water, the dried iris-root yields a product of a light-yellow colour, of an unctuous consistence, and smelling of violets. This substance, according to Dumas, has the formula $C_8H_8O$, and he considers it to be an oxide of the essence of roses. When purified by repeated crystallisations from alcohol, it loses its smell, and when then dissolved in alcohol, exhibits an acid reaction: it melts at 52°. The analyses of this substance show it to be myristic acid, $C_{14}H_{28}O_2$. The presence of a fatty acid having been then ascertained, the crude product was saponified, and the acid separated by acetic acid. The crude product appears to consist of myristic acid to the amount of 1 per 1,000 of the root, mixed with an ethereal oil present to the amount probably of less than $\frac{1}{10000}$th; and this oil is apparently due to fermentation, as the living roots show no trace of it. The myristic acid appears also to be formed by the action of the water during distillation, as no free acid could be detected in the roots themselves, after treatment with carbon disulphide; but whether when large quantities are worked with, free acid may not be found, is not certain, the author, owing to the costliness of the material, not being able to obtain large quantities.

E. W. P.

## Reactions of Animal and Vegetable Albuminoïds. By Th. Weyl (Pflüger's Archiv., xii, 635—638).

I. *Animal Albuminoïds.*—1. Vitellin, from white of egg, is soluble in dilute solution of sodium chloride, but coagulates when this solution is heated to 75°. If the temperature be raised slowly, coagulation begins at 70°; but when rapidly heated, not till a temperature of 80° is reached. A body agreeing in all respects with the above, was obtained from liquor amnii.

Vitellin, when dissolved in sodium chloride and precipitated by addition of water, changes on long standing in water into an albuminate (casein). It is then insoluble in solution of sodium chloride, but is

completely soluble in a 1 p.c. solution of sodium carbonate. If freshly precipitated vitellin be dissolved in a 1 p.c. solution of sodium carbonate, this solution is difficultly precipitable by water alone, but is abundantly precipitated on passing carbonic acid gas into the liquid. If, after a short suspension of the vitellin in water, it be attempted to dissolve it in sodium carbonate solution, a singular phenomenon occurs. The liquid becomes, for a few moments, clear, but then becomes gradually more and more turbid, until apparently it is as turbid as it was originally. The precipitate may then be filtered off, when the filtrate will be found to give scarcely any turbidity with acetic acid and potassium ferrocyanide. A fresh addition of $Na_2CO_3$ solution causes a renewed precipitation; and this reaction may be repeated several times, provided that the solution of soda be not too concentrated.

2. Myosin, dissolved in dilute solutions of sodium chloride, then precipitated by the addition of water, and redissolved in NaCl solution, coagulates at 55—60° in a neutral solution.

3. Fibrino-plastic substance, prepared by diluting blood with 15 volumes of water, precipitated by the addition of a few drops of acetic acid, and the passage of a stream of carbonic acid through the solution, and then dissolved in NaCl solution, coagulates in its neutral solution at 75°. Further experiments are required to determine whether this difference in the coagulating points of myosin and fibrino-plastic substance is constant. When dissolved in NaCl solution, both substances are precipitated on saturation with NaCl.

4. The alkali albuminate of Kühne, obtained from blood, by treatment with carbonic acid and acetic acid, and the substance obtained by treating blood with $CO_2$ alone (paralbumin + globulin, Kühne), must be regarded as identical. They both coagulate at 75°.

II. *Vegetable Albuminoïds.*—1. The existence of soluble albuminoïds in plants, similar to egg-albumin, has not been demonstrated.

2. Globulin substances, similar in their reactions to animal albuminoïds, may be extracted from a variety of seeds.

3. A vegetable vitellin, similar to animal vitellin, and coagulating at 75°, may be extracted from maize, peas, &c.

4. From the same plants, a vegetable myosin may be obtained, coagulating at 55—60°.

5. A. Schmidt's legumin is a mixture of the above bodies, myosin and vitellin.

6. The above-named seeds yield casein-like bodies (albuminates); but only when they have undergone change, *e.g.*, become rancid.

7. The vegetable albuminoïds are converted by acids and alkalis into alkali or acid-albumin (syntonin).

8. Vegetable globulin, when precipitated and allowed to stand under water, becomes insoluble in sodium chloride solution, but dissolves in a 1 p.c. solution of sodium carbonate. The globulin is then converted into an albuminate.

9. After some time, the above albuminate (casein), under the influence of water, becomes insoluble in very dilute solution of hydrochloric acid, and is then indistinguishable from coagulated albuminoïds.

10. The globulin obtained from peas, &c., by extraction with

sodium carbonate and precipitation with water and carbonic acid, behaves with sodium carbonate, &c., exactly like animal vitellin.

T. S.

### On the Spectroscopy of Blood-pigments. By C. GÄUGE (Deut. Chem. Ges. Ber., ix, 833).

ALKALINE solutions of blood and indigo show the same absorption-spectra under certain conditions, viz., when the blood-colouring matter has been reduced by a small quantity of a sulphite, and when an alkaline solution of so-called indigo-carmine is used, consisting chiefly of cœrulin- and phœnicin-sulphonates, and termed by Berzelius "purpurinsulphuric acid." Blood solutions which have not been reduced, exhibit a band in a different position, which disappears on cooling the liquid; and those which have been reduced show the same spectrum, whether the solution be warm or cold; whilst the bands of purpurin-sulphuric acid fade on cooling, and are completely destroyed by boiling with concentrated alkalis, the colours not being restored by ammonium sulphide. Vogel appears to have been led into an error with reference to the permanence of the blood spectrum on cooling, inasmuch as the oxygenised colouring matter becomes reduced by heating with potash, the albumin of the blood being altered and very probably its sulphur being withdrawn, whence the reducing action.

C. R. A. W.

## Physiological Chemistry.

### On Glycogen from the Human Liver. By E. KÜLZ (Pflüger's Archiv. f. Physiologie, xiii, 267—269).

A PATIENT suffering from acute diabetes died 34 hours after last partaking of nourishment. The "post-mortem" was made 12 hours after death. About $\frac{1}{10}$th of the liver having been cut into cubes, was boiled with water for 1 hour. The filtrate, which reduced copper-solution, was concentrated, cooled, and precipitated with hydrochloric acid and potassio-mercuric iodide. The resulting precipitate was rapidly filtered off, and to the filtrate from 2—3 times its volume of 96 per cent. alcohol added. A precipitate ensued, which, after washing and drying at 110° C., weighed 0·6850 gram. This, after purification, formed a sparkling white powder, free from nitrogen and ash, dissolving in water with opalescence, and giving with iodine the characteristic colour of glycogen.

F. J. L.

## Is Grape-sugar a Normal Constituent of Urine?

By E. KÜLZ (Pflüger's Archiv. f. Physiologie, xiii, 269—271).

AN attempt to isolate grape-sugar from 100 litres of normal urine, by a modification of Brücke's method, did not give positive results.

F. J. L.

## The Elimination of Acids through the Kidneys.

By R. BUCHHEIM (Pflüger's Archiv., xii, 326—332).

IN order to investigate the cause of the acidity of the urine, Fr. Hofmann fed a pigeon for 28 days upon yolk of egg, which is an acid substance, and leaves an intensely acid ash. The ash of the excrement was intensely acid, and its constituents absolutely and relatively the same as in the ash of the food. This seemed to prove the power of the body to retain its alkalis; and that the greater part of the uric acid must have left the body in the free state. He thought that the acids formed in the body by decomposition do not immediately enter into combination with the alkaline salts of the blood, but that they pass into the kidneys and are excreted into the urine before such combination takes place.

Buchheim contests this view. He thinks that Hofmann's explanation is untenable. It would not account for the known effects of acid poisoning, nor for the results obtained by Gaethgens upon introducing acids into the stomach. The author, therefore, considers that as the blood contains, under the most varying conditions, a very constant quantity of mineral substances, these exist in definite combination with the albuminoïds of the body. This view is supported by the fact that the salts of the heavy metals are decomposed by albumin, and that the acid albuminate is easily separated from the basic albuminate by diffusion; the salts of the alkalis would probably behave in a similar manner. The organs which bring about this dissociation have, however, yet to be discovered.

T. S.

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## The Regulation of Animal Temperature in the Mammalia.

By E. PFLÜGER (Pflüger's Archiv., xii, 333—336).

A PRELIMINARY notice, attempting to prove that the amount of dissociation of living material in warm-blooded animals is proportional to the temperature of the organs.

T. S.

## The Poisonous Nature of the Extract from the Human Corpse.

By A. MORIGGIA and A. BATTISTINI (Gazzetta chimica italiana, v, 472—478).

THIS paper contains the details of 47 experiments made to ascertain whether any alkaloïd could be extracted from the dead human subject in various stages of decomposition, which would account for the poisonous effects produced when an extract of it is administered to a

living animal. Extracts from five subjects, prepared in different ways similar to those ordinarily employed for extracting alkaloïds in toxicological examinations, were administered to Guinea pigs and to frogs both internally and by subcutaneous injection. From the results obtained the authors conclude that the cadaverous poison is more abundant in putrid subjects than in fresh ones, and is as deadly as curarine or the more powerful alkaloïds. It is also shown that the effects could not be due to extractive substances such as leucine, creatine, taurine, &c., which are insoluble in water and in ether, nor to living germs, but to fixed chemical compounds hitherto uninvestigated. Of these, some are extracted by the solvents employed, whilst others remain behind dissolved in the aqueous fluids of the viscera. The best solvent to extract the cadaverous poison, as also the poisonous alkaloïds, is amylic alcohol. It would appear that this putrefactive poison no longer exists in the subject seven months and a half after death.

C. E. G.

### Some Unorganised Ferments of the Animal Organism.

By P. Grützner (Pflüger's Archiv., xii, 285—307).

In operating with saliva and starch, the author has confirmed the observation that the nature of the products formed varies with the relative quantities of the ferment and material operated on. When the proportion of ferment is small, erythrodextrin is the chief product; but when the quantity of ferment used is large, sugar is the main product of the action. The diastatic ferments vary in their actions according to the intensity of the fermentative change going on.

Further, changes in the process of fermentation produced by pepsin, by whatever means (cold, paucity of the ferment, chemical agents) brought about, give rise to the formation of varying products of fermentation. It was also found that the unorganised ferments are not capable of determining the metamorphosis of an unlimited quantity of fermentable substance, but that they are themselves destroyed to an appreciable extent during fermentation.

Grützner likewise asserts that the central portion of the pancreatic cells acts not only as an albumin-ferment, but that it is also capable of acting as a diastatic and fat ferment.

T. S.

## Chemistry of Vegetable Physiology and Agriculture.

### Contributions to the Chemical Knowledge of Culinary Plants.

By Dahlen (Dingl polyt. J., ccxi, 91—92.).

The following analytical results are taken from Dahlen's investigations on pot-herbs (Landwirthschaftliche Jahrbücher, 1875, pp. 613—723.)

*Sprouts.*—The young suckers of sprouts and of asparagus can be regarded only as luxuries.

*Culinary and Potage Herbs.*—The various kinds of cabbages form an excellent nutrient rich in albumin and phosphóric acid. The most proteïnaceous are the small heads of the rose cabbage, which approach most nearly to the undeveloped heads of cauliflowers. The leaves of white cabbage also form an excellent nutriment. The same may be said of the leaves of spinach, which contain much albumin and mineral nutrients.

*Salad Herbs.*—These, like the various kinds of cabbage, are very rich in nitrogen, ash, and phosphoric acid. In the fresh state they contain about 94 per cent. of water and 2 per cent. of nitrogenous bodies.

*Roots, Tubers, and Tuberous Root-stocks* are generally characterised by their small amount of nitrogen and phosphoric acid. They contain, with but little crude fibre, a large quantity of extractives free from nitrogen; also about 84—94 per cent. of water.

*Onions* contain a sulphurised, readily volatile, strongly smelling oil.

*Fruits and Seeds* are the most valuable part of the vegetable nutrients, as they contain a large quantity of proteïn substances. Cucurbitaceous plants form two classes, one comparatively rich, the other comparatively poor in proteïn. The cucumbers belong to the former class of plants, and form in a certain stage of development a nutrient very rich in albumin, phosphoric acid, and potash. Proportion of nutrient, 1 : 1·5. They also contain much grape-sugar.

*Melons* contain phosphoric acid, also 1·3 per cent. of a liquid orange-coloured fat, and in the fresh state about 95 per cent. of water.

*Gourds* are poor in proteïn and phosphoric acid. Proportion of nutrient 1 : 6 to 1 : 8.

The fruits of the tomato (a solanaceous plant) rich in fat and grape-sugar, contain much proteïn.

*Legumes* contain the largest quantities of proteïn, starch, potash, and phosphoric acid. The legumin forms the main ingredient of the albuminous bodies contained therein. The increase of seeds also increases the contents of nutrients. As the seeds ripen the sugar is replaced by starch, and the quantities of fat, woody fibre, and water are decreased.

*Juicy Fruits and Berries* form non-albuminous eatables, which are valued only on account of their agreeable taste.

D. B.

## On the Alcoholic and Acetic Fermentation of the Fruits, Flowers, and Leaves of certain Plants. By S. de Luca (Compt. rend., lxxxiii, 512—514).

It has been established by numerous experiments that the saccharine matter of fruit, kept from contact with air, undergoes a species of fermentation, and is converted into carbonic acid and alcohol, without the production of alcoholic or acetic ferment. This transformation is slow, and is attended with evolution of nitrogen and sometimes of hydrogen; but it takes place less readily when the products of transformation are not removed from the sphere of action. Leaves

and flowers act like fruit in a limited atmosphere of carbonic acid, hydrogen, or air, or even in a vacuum, or in hermetically sealed vessels. Fruit is converted into a gelatinous brown mass. This decomposition is evidently due to the fermentation of mannite, and plants containing this sugar evolve hydrogen along with the other products.

W. R.

## Reduction of Nitrates by Bacteria. By E. GRIESSMAYER (Deut. Chem. Ges. Ber., ix, 835).

FRESH maple leaves digested with water gave a liquid apparently containing both ozone and hydrogen peroxide, as it rendered guaiacum tincture blue and readily decolorised permanganate solution. Guaiacum and malt extract, also potassium dichromate and sulphuric acid, gave no result. Fehling's solution and alkaline indigo liquor were quickly reduced, but basic bismuth salts did not react, whence no grape-sugar could have been present.

Leaves which had been strongly insolated gave no blue with iodine and starch, and only furnished a blue with guaiacum after ten minutes; on the other hand, the presence of hydrogen peroxide was distinguishable by means of iodide and starch with ferrous sulphate, by Struve's lead dioxide reaction, by permanganate, and by ferricyanide and ferric chloride. On referring to Schönbein's paper in *Erdman's Journal*, vol. 105 (1868), the author found the title to be "On the Conversion of Nitrates into Nitrites by Confervæ and other Organic Bodies," amongst which are mentioned blood corpuscles, urinary fungus, yeast, mould, and especially the organisms found in drinking-water; wherefore Schönbein must be regarded as having first called attention to the reduction of nitrates by bacteria.

C. R. A. W.

## On the Disappearance of Ammonia contained in Natural Waters. (Part I.) By A. HOUZEAU (Compt. rend., lxxxiii, 525—527).

SPRING and river waters contain a comparatively small proportion of ammonia, while atmospheric water is sometimes very rich in ammonia. Does the ammonia disappear from the water after it has reached the ground? After standing for two months, a water which contained at first 7·3 milligrams of water per litre contained 0·4 milligram. Other experiments were made with the same result, showing distinctly that ammonia is lost. From other experiments it appears that light takes part in the production of this phenomenon, but is not indispensable. It is not necessary to expose the water to air, for the ammonia disappeared even in a stoppered tube. Ammonia added to water which is allowed to stand also disappears after some time. The author in his next communication purposes to ascertain what becomes of this ammonia.

W. R.

# Analytical Chemistry.

## An Apparatus for the Determination of Nitrogen.

By KARL ZULKOWSKY (Liebig's Annalen, clxxxii, 296—304).

THE construction and use of this apparatus cannot be satisfactorily explained without the aid of the drawings which accompany the original paper. It is a contrivance for working the process of Dumas without the use of mercury. The preliminary testing of carbon dioxide for air is done in the measuring apparatus, and the waste of potash-solution and the disagreeable wetting of the hands with that liquid, incident to the process as ordinarily conducted, are thereby avoided. The results obtained with it are accurate.

J. R.

## Analysis of the Saltpetre used for the Manufacture of Gunpowder.

By R. FRESENIUS (Zeitsch. Anal. Chemie, 1876, 65—68).

THE potassium nitrate furnished to the powder-manufactories has, as a rule, so high a degree of purity, that only a trifling amount of chlorine can be detected by the direct addition of reagents. The addition of ammonium oxalate, or ammonium phosphate with ammonia often fails to precipitate the traces of lime and magnesia which are generally present, and the determination of the very small quantity of sodium proves even still more difficult.

As the analyst is now frequently required to determine these traces of foreign salts in different kinds of nitre, the author publishes the method of procedure which from long experience he has found to give the most accurate results.

1. *Determination of the Water.*—This is done in the usual way by ascertaining the loss on heating a weighed portion in a platinum crucible. The temperature may be gradually raised until the salt just begins to melt.

2. *Determination of the Chlorine and of the Residue Insoluble in Water.*—100 grams are dissolved in hot water, and the residue collected and weighed on a tarred filter. The filtrate is acidified with pure nitric acid, mixed with silver nitrate, and kept for some time in the dark at a gentle heat. The precipitate is then collected on a small filter, and determined either directly as silver chloride, or by reduction to metallic silver.

3. *Determination of the Lime, Magnesia, and Soda.*—100 grams of salt are dissolved with 1·5 grams of potassium chloride, in about 100 c.c. of water; the solution is then mixed with about 500 c.c. of pure alcohol of 96 per cent., well stirred, and the crystalline residue separated by filtration, and washed with alcohol. The filtrate is then evaporated to dryness, the residue dissolved in a little water, and the solution treated as before with alcohol, and filtered. This having been again repeated, an alcoholic solution is obtained, containing all the lime, magnesia, and soda, but only a small quantity of potassium. This solution is now evaporated to dryness, and the residual salts con-

verted into chlorides by digestion with hydrochloric acid, after which the lime can be separated by ammonium oxalate, and the magnesia by ammonium phosphate. The filtrate freed from lime and magnesia is now heated in a platinum basin to expel ammonia, one or two drops of ferric chloride added, and afterwards ammonia or ammonium carbonate to slight alkaline reaction; the liquid is then warmed, the basic phosphate of iron filtered off, and the filtrate evaporated to dryness, and heated until the ammonium salts are expelled. From the residue the potassium is separated as potassio-platinic chloride, the alcoholic filtrate evaporated to dryness, and the sodio-platinic chloride, together with the excess of the platinum salt, decomposed by careful heating in a stream of hydrogen-gas. Finally, the sodium chloride is extracted with water, the solution evaporated to dryness, and the sodium calculated from the weight of the residue.

An actual analysis gave:—

| $KNO_3$. | $NaNO_3$. | $Mg(NO_3)_2$. | $Ca(NO_3)_2$. | NaCl. | Insoluble. | Moisture. |
|---|---|---|---|---|---|---|
| 99·8124 | 0·0207 | 0·0093 | 0·0006 | 0·0134 | 0·0210 | 0·1226 = 100 |

H. H. B. S.

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**A False Reaction of Nitric Acid.** By G. C. WITTSTEIN (Zeitsch. Anal. Chemie, 1876, 61—65).

A MODIFICATION of the potassium iodide and starch test for the detection of nitrites in drinking water was published by Kämmerer. He added, in addition to the foregoing reagents, acetic acid and sodium bromate, affirming that the violet colour indicative of the presence of nitrous acid could be produced in this way, in solutions twice as dilute as those required to give the same indication without the use of sodium bromate. This supposed reaction evidently rests upon the supposition that nitrous acid reduces sodium bromate or bromic acid more easily than it decomposes potassium iodide, so that the bromine set free can in in its turn decompose the potassium iodide, and thus give rise to the production of the blue colour.

The test, if made in this way, is however utterly fallacious, since the blue colour is produced quite the same without the addition of any nitrite whatever, and it is only necessary to add to some distilled water a little starch-paste, potassium iodide, sodium bromate, and a few drops of acetic acid, to show this to be the case; the change which takes place being according to the following equation:—

$$NaBrO_3 + 5KI + 6\left\{\begin{matrix}CH_3\\COHO\end{matrix}\right. = \left\{\begin{matrix}CH_3\\CONaO\end{matrix}\right. + 5\left\{\begin{matrix}CH_3\\COKO\end{matrix}\right. + Br + 5I + 3H_2O.$$

H. H. B. S.

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**Can the Indirect Methods for the Determination of the Alkalis be made either to check each other, or to serve as a Check upon the Direct Methods?** By M. KRETSCHY (Zeitsch. Anal. Chemie, 1876, 37—57).

THE author examined the three following methods for the indirect determination of potash and soda:—

I. By the conversion of an accurately weighed quantity of the mixed chlorides into sulphates.

II. By the determination of the sum total of the mixed chlorides and the chlorine contained in them.

III. By the determination of the sum total of the mixed sulphates and the sulphuric acid contained in them.

The results were as follows:—

I. *By the Conversion of the Chlorides into Sulphates.*

Formula. If $c$ = the sum of chlorides
and S = that of the sulphates,
then the KCl = $26{\cdot}18803\,c - 21{\cdot}55317$ S.

| Quantities taken in milligrams. | Proportion of KCl to NaCl. | Sulphates. Calculated. From atomic weights given by Fresenius. | Sulphates. Calculated. From atomic weights of Stas. | Sulphates. Found. | Difference between the numbers in the previous column and those calculated from the atomic weights of Stas. | Value of this difference in milligrams of KCl. |
|---|---|---|---|---|---|---|
| I .. KCl .. 17·5, NaCl .. 503·2 | 1 : 28 | 631·58 | 631·86 | 632·05 | + 0·19 | − 4·0 |
| II .. KCl .. 21·6, NaCl .. 501·65 | 1 : 23 | 634·48 | 634·76 | 634·6 | − 0·16 | + 3·6 |
| III. KCl .. 19·5, NaCl .. 305·7 | 1 : 15 | 394·05 | 394·227 | 394·1 | − 0·12 | + 2·7 |
| IV. KCl .. 19·15, NaCl .. 382·2 | 1 : 19 | 486·55 | 486·76 | 486·75 | − 0·01 | + 0·3 |
| V .. KCl .. 9.9, NaCl .. 240 | 1 : 24 | 303·04 | 303·179 | 303·2 | + 0·02 | − 0·4 |
| VI. KCl .. 3·95, NaCl .. 70·25 | 1 : 17 | 89·94 | 89·98 | 89·95 | − 0·03 | + 0·7 |
| VII KCl .. 13·08, NaCl .. 54·96 | 1 : 4 | 82·03 | 82·07 | 82·05 | − 0·02 | + 0·4 |

The maximum difference was therefore less than 0·2 mgrm., yet even this when calculated into potassium chloride introduces an error of − 22·6 per cent.

II. *From the weight of the Sulphates and the Sulphuric Acid contained in them.*

Formula. If S = the sum of the sulphates
and $s$ = the sulphuric acid,
then the $K_2SO_4$ = $5{\cdot}407213$ S $- 9{\cdot}59778\,s$.

| Quantities taken in milligrams. | Proportion of potassium to sodium salt. | Sulphates by calculation. | Barium sulphate. | | | Value of difference | | Remarks. |
|---|---|---|---|---|---|---|---|---|
| | | | Calculated. | Found. | Difference. | in $SO_3$. | in $K_2SO_4$. | |
| I ..... { KCl ..... 21·6<br>NaCl ..... 501·65 } | 1 : 23 | 634·48 | 1033·44 | { 5th weighing 1032·8<br>1st ,, 1042·2 } | − 0·6 | − 0·22 | + 2·17 | |
| II..... { KCl ..... 3·95<br>NaCl ..... 70·25 } | 1 : 17 | 94·91 | 146·13 | { 3rd ,, 144·7<br>1st ,, 148·2 } | − 1·43 | − 0·49 | + 4·72 | |
| III .... { KCl ..... 19·5<br>NaCl ..... 305·7 } | 1 : 15 | 394·05 | 639·66 | { 5th ,, 639·27<br>1st ,, 645·2 } | − 0·39 | − 0·13 | + 1·3 | |
| IV .... { KCl ..... 13·08<br>NaCl ..... 54·96 } | 1 : 4 | 82·03 | 129·97 | { 2nd ,, 128·2<br>1st ,, 128·9 } | − 1·75 | − 0·60 | + 5·7 | |
| V..... { $K_2SO_4$ ..... 4·3<br>$Na_2SO_4$ ..... 244·1 } | 1 : 56 | 248·4 | 406·28 | { 2nd ,, 406·0<br>1st ,, 408·0 } | − 0·28 | − 0·09 | + 0·9 | Excess of barium chloride. |
| VI .... { $K_2SO_4$ ..... 109·7<br>$Na_2SO_4$ ..... 98·7 } | 1·11 : 1 | 208·4 | 312·0 | 1st ,, 309 | − 2·8 | − 0·96 | + 9·2 | 0·081 |
| VII .... { $K_2SO_4$ ..... 99·2<br>$Na_2SO_4$ ..... 88·7 } | 1·19 : 1 | 187·9 | 268·36 | { 2nd ,, 267·1<br>1st ,, 267·3 } | − 1·26 | − 0·43 | + 4·3 | 0·122 |
| VIII .. { $K_2SO_4$ ..... 170·7<br>$Na_2SO_4$ ..... 128·2 } | 1·3 : 1 | 298·9 | 438·64 | 1st ,, 434·85 | − 3·8 | − 1·3 | + 12·5 | 0·128 |

The sulphuric acid was determined as barium sulphate according to Bunsen's directions, the precipitate being considered clean when the difference between two weighings amounted to *not more* than 0·5 mgrm. This rule was, however, departed from in those cases when, after repeated digestion, the precipitate continued to lose more than 0·5 mgrm., although no barium chloride could be detected in the washings.

III. *From the Weight of the Chlorides and the Chlorine contained in them.*

Formula. If C = the sum of the chlorides
and $c$ = the quantity of chlorine,
then the KCl = $4{\cdot}634894\,C - 7{\cdot}647047\,c$.

| Quantities of the chlorides in milligrams. | | | Proportion of NaCl to KCl. | Silver chloride. | | |
|---|---|---|---|---|---|---|
| | | | | Calculated. | Found. | Error. |
| I ..... | KCl ..... | 35·472 | 1 : 7 | 722·79 | 722·77 | − 0·02 |
| | NaCl ..... | 267·069 | | | | |
| II..... | KCl ..... | 10·679 | 1 : 9 | 261·598 | 261·54 | − 0·05 |
| | NaCl ..... | 98·353 | | | | |
| III .... | KCl ..... | 5·325 | 1 : 83 | 1094·509 | 1094·61 | + 0·1 |
| | NaCl ..... | 451·632 | | | | |
| IV .... | KCl ..... | 4·430 | 1 : 61 | 681·320 | 681·23 | − 0·09 |
| | NaCl ..... | 274·494 | | | | |
| V..... | KCl ..... | 4·568 | 1 : 81 | 916·239 | 916·2 | − 0·04 |
| | NaCl ..... | 370·23 | | | | |
| VI .... | KCl ..... | 2·371 | 1 : 51 | 301·400 | 301·50 | + 0·1 |
| | NaCl ..... | 121·107 | | | | |
| VII.... | KCl ..... | 1·743 | 1 : 271 | 1164·82 | 1164·73 | − 0·09 |
| | NaCl ..... | 473·866 | | | | |

Since 1 mgrm. AgCl = 0·247 Cl, the error in chlorine is not more than 0·03, or in potassium chloride 0·2 mgrm. It will be seen from the formulæ that, in the 1st method an error of 0·1 mgrm. in the sulphates corresponds to 2·5 mgrms. KCl, and in the 2nd method 0·1 mgrms. in the sulphuric acid to 0·95 mgrms. $K_2SO_4$; thus the determinations made in exactly the same mixtures by the 1st and 2nd methods may be thus stated:—

| | By conversion into sulphate. | Error per cent. | From the determination of sulphuric acid. | Error per cent. |
|---|---|---|---|---|
| KCl ..... 21·6<br>NaCl ..... 501·65 | 25·2 KCl | + 16·6 | 23·4 KCl | + 8·4 |
| KCl ..... 19·5<br>NaCl ..... 305·7 | 22·2 „ | + 13·8 | 20·6 „ | + 5·6 |
| KCl ..... 13·08<br>NaCl ..... 54·96 | 13·4 „ | + 2·4 | 18·0 „ | + 43·7 |
| KCl ..... 3·95<br>NaCl ..... 70·25 | 4·6 „ | + 17·2 | 7·9 „ | + 100 |

In the third method an error of 0·1 mgrm. in the chlorine corresponds to 0·76 mgrms. KCl, so that in seven experiments the error did not exceed 0·03 Cl or 0·2 KCl.

Some experiments were also made upon the determination of the alkalis in the direct way, by means of platinic chloride. In six experiments out of ten the KCl was found with almost absolute accuracy, and in neither of the remaining four did the error reach 0·4 mgrm.

Finally, details are given of some experiments upon the effect of heat upon mixtures of the chlorides of magnesium, potassium and sodium, with free access of air.

The author draws the following conclusions:—

1. The indirect methods are untrustworthy unless there is absolute proof of the purity of the mixed salts. With mixtures of pure salts, the chlorine method gives the most accurate results; the sulphuric acid methods are even then untrustworthy: that depending on the conversion of the chlorides into sulphates, because the error becomes multiplied by 21·5; and that which is based upon the determination of the sulphuric acid, because when the potash salt is present in larger quantities, the error is greater and more uncertain.

2. In the chlorine method, and that by the conversion of the chlorides into sulphates, the error due to the relative quantities of the two salts is no greater than that occasioned by the variations in the atomic weights. In the method by the determination of sulphuric acid, the relative proportions in which the two salts are present exercises a decided influence upon the result. If the sodium salt preponderates by 15 to 20 times, the error in the barium sulphate amounts only to a few tenths of a milligram, whereas if the potassium salt nearly equals or exceeds the sodium salt, the error becomes increased to several milligrams.

3. The indirect methods cannot serve for mutual verification.

4. If the chlorine method is used alone, absolute proof of the purity of the alkalis must be established; but on the other hand, if the potassium be determined also in the direct way, then the chlorine

method furnishes a delicate indication of the purity of the mixed salts.

5. Potassium chloride in quantities of from 0·003 to 0·120 grm. can be determined extremely accurately by means of platinic chloride, if the $2KCl,PtCl_4$ is reduced, and the KCl washed out, and separately weighed.

6. This exact potash determination, taken in connection with the chlorine method, renders it possible to determine sodium chloride also with considerable accuracy, when traces of other substances are present.

7. If traces of magnesia are suspected, the mixed chlorides must be kept at a dull red heat for an hour or so previous to the determination of the chlorine.

8. Under the action of heat magnesium chloride is decomposed and converted into the oxide; the product, however, always shows a chlorine reaction, though the quantity of silver chloride precipitated may not be weighable.

H. H. B. S.

## Determination of Sulphur in Coal Gas.

(Dingl. polyt. J., ccxxi, 94).

VOGEL showed in 1853 that coal gas contains carbon disulphide, which he determined by passing the gas over a copper-spiral. Herzog proposed for the determination of this compound an ammoniacal alcoholic lead solution. A. W. Hofmann determined the sulphur by burning the gas in air and condensing the sulphurous acid formed. Evans and Letheby constructed peculiar apparatus for its determination.

Brügelmann burns the gas in oxygen and determines the sulphuric acid formed by passing the gas through a combustion tube filled with a 10 cm. long layer of granulated lime. The lime is afterwards dissolved in water and an acid, and the sulphuric acid determined as $BaSO_4$.

D. B.

## Chrome Ore Analysis. By R. KAYSER

(Zeitschr. Anal. Chem., 1876, 187—188).

ONE part of very finely powdered ore is heated to bright redness for about an hour, in an open crucible, with repeated stirring, together with two parts of pure calcined soda, and three parts of calcic hydrate. The latter is prepared by adding to burned marble, water sufficient to cause it to fall to powder. After cooling, the chromate is dissolved out with hot water.

M. M. P. M.

## Contributions to the Analysis of Iron. By

(Dingl. polyt. J., ccxx, 534—537).

WITH regard to the direct weighing of the molybdate precipitate (mentioned 1875, ccxviii, 492), the author says that the results were the

same as those obtained by weighing the magnesium salt. It was found, however, that Munktell's Swedish filter paper contained phosphoric acid (a paper 80 mm. in diameter gave 6 mg. of precipitate); such paper must therefore be treated with dilute nitric acid before using it.

*Estimation of Carbon.*—Wöhler and Ullgren's methods have been employed by the author. If the iron is easily powdered very finely, the mixing with powdered cupric oxide and combustion in oxygen is the most satisfactory method. If, as in most cases, this method cannot be applied, Ullgren's method (treatment of the iron with cupric sulphate, or chloride and oxidation of the residue with chromic and sulphuric acid) is the quickest and best. After having added the copper the solution is not, as Fresenius recommends, poured off, but filtered through an asbestos filter, the last traces of liquid being removed by an air-pump. The contents of the filter are next brought into the oxidizing flasks, and the latter connected with the absorbing apparatus. The author uses a small condenser, which surrounds the upper bulb of the oxidizing flask; in this way the oxidation can, after a few minutes, be carried on at a fast boiling heat, the stem being cooled to such an extent that a film of moisture is not even perceived in the tube connecting the flask and the drying tube. For absorbing the $CO_2$ evolved, a tube filled with soda-lime is used. It was found that drawing 5—6 litres of air through the apparatus after boiling, was not sufficient to clear the apparatus; twice that quantity had to be used. Eggertz's colorimetric method did not give good results.

*Estimation of Silicon.*—By dissolving the iron in nitric acid of 1·20 sp. gr., and evaporating and igniting in a platinum dish, the silicic acid was rendered insoluble, and remained behind with the graphite on treatment with hydrochloric acid. The residue was dried, put into a platinum crucible, pressed into a powder by means of a platinum spatula, and the graphite burnt, partly covering the crucible with the lid. In all manuals we find the statement that this graphite residue can be burnt in oxygen only when the strongest red heat is applied. At the same time the author thinks it very strange, that the fact *that the graphite in the above mentioned process (combustion of 4 grams of iron in 30—40 minutes) is completely burnt if heated over a simple Finkner's lamp, and that the silicic acid is left behind perfectly pure and white*, has not been mentioned anywhere.

*The determination of the sulphur* is made according to Johnston's method, by passing the hydrogen sulphide evolved from the iron by hydrochloric acid into brominated hydrochloric acid, having expelled the air with pure hydrogen. 6 grams of raw material are used, treated with 20 c.c. of water and 60—70 c.c. of concentrated hydrochloric acid, and the gas passed into a Will's nitrogen apparatus containing hydrochloric acid saturated with bromine. The further details are those already described.

D. B.

## Combustion of Organic Substances in Oxygen.

By D. LOISEAU (Compt. rend., lxxxii, 1339—1341).

THIS paper gives in tabular form the results of 18 analyses of sugar made by burning that substance in pure oxygen in tubes of various diameters. From these results the author concludes that organic substances may be burned, with an exactitude which leaves nothing to be desired, in tubes 15 mm. or more in diameter, in a current of oxygen passing at the rate of $1\frac{1}{4}$ to $1\frac{1}{2}$ litres per hour. The combustion in oxygen alone is as complete as in oxygen used in conjunction with cupric oxide.

J. R.

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## Spectroscopic Method of Discovering minute quantities of the Vapour of Hydrocarbons in a Gaseous Mixture.

By A. and G. DE NEGRI (Gazetta chimica italiana, v, 438).

IF the gaseous mixture, which must be free from oxygen, carbonic oxide, and carbonic acid be introduced into a Geissler's tube, or the vacuum of a barometer, and the electric spark passed (the pressure must be less than 20 millimeters), the discharge has a bluish colour, and when examined spectroscopically, shows the carbon spectrum with great intensity. By examining the gases dissolved in water, indirect evidence may be obtained of the evidence of a hydrocarbon, if such be present.

C. E. G.

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## Analysis of Coal for Practical Purposes.

By G. C. WITTSTEIN (Pharm. J. Trans. [3], vii, 92—94).

THE question whether a given specimen belongs to the class of pit coals or to the class of lignites can be satisfactorily answered by the following tests. If by heating a small portion of the powdered coal with 5 grams of caustic potash for several minutes, the latter after cooling remains colourless, or becomes but slightly yellowish, the coal belongs to the class of pit coals. Should the alkali, on the contrary, turn dark brown or opaque, the coal examined is lignite. This process, though quite old, has never been surpassed by any of the more recent methods in which the coal is subjected to dry distillation, the distillate thus obtained from lignites containing considerable quantities of acetic acid, whereas that of pit coals is entirely destitute of it. The distinction between the quantities of sulphur contained in lignites and in pit coals is not very satisfactory.

The total analysis of coal may be divided into four principal operations, for each of which a separate quantity of the sample is weighed out immediately after receipt, as coal always loses weight on exposure to air.

I. *Determination of Sulphur.*—1 gram of the well pulverized sample is mixed with 4 grams potassium nitrate, and 2 grams anhydrous sodium carbonate, and the mixture transferred in small quantities at a time to a silver or platinum crucible of 30 grams capacity, the bottom of which has been heated to low redness. The lid must be put on after

each addition. Having introduced the whole of the mixture, the lid is replaced, and the liquid heated for at least a quarter of an hour to a lively redness. The contents of the crucible when cold are treated with water, and the solution is supersaturated with hydrochloric acid. To the solution (filtered if necessary) barium chloride is added, and the sulphur is estimated from the barium sulphate obtained. Some lignites show as much as 7 per cent of S, whereas pit coals contain as little as $\frac{1}{4}$ per cent. Coals absolutely free from sulphur have never been met with. Since the solution contains much nitric acid, the $BaSO_4$ precipitate must be freed from adhering barium nitrate with hydrochloric acid. The sulphuric acid present in the coal is left in the ash, and is therefore passive or indestructive; its quantity deducted from the total sulphur gives the amount of active or destructive sulphur present.

II. *Determination of Water and Ash constituents.*—10 grams of the powdered coal are placed in a platinum crucible in an air-bath, and heated to about 120° for two hours, till on holding a plate of glass over the open tubulure of the bath, a film of moisture is no longer formed. The loss in weight is water. From the external appearances of coal, and the large quantities of water in some samples (20 per cent. was not unfrequent, 30 or even 35 per cent. sometimes occurred, at other times as little as 2 per cent.), it may be inferred that the water in coal does not merely adhere mechanically, but is chemically bound, however weak this union may be. The sample is next ignited for determining the ash, the lid being kept on the crucible until the escape of volatile matter is no longer apparent. When cold the residue is weighed as ash. It will either have the appearance of a dense, porous, apparently molten mass—caking coal—or will be but slightly coherent, cinder coal, or will remain powdery—sand coal. The quantity of ash varies as widely as the moisture. The ash is introduced into a small flask, and digested with HCl (1·17 sp. gr.) for two hours. The undissolved silica is separated by filtration, and the sulphuric acid in the filtrate determined as barium sulphate. To the filtrate of the sulphate sulphuric acid is added, and the filtrate from the latter tested with hydrogen sulphide. If copper is present, the solution is completely precipitated with hydrogen sulphide, and the precipitate weighed after ignition as cuprous sulphide. The iron in the filtrate will in this case have been reduced to a ferrous salt. It is therefore necessary to oxidize the solution with nitric acid, after which ammonia may be added. In the precipitate alumina and phosphoric acid are separated from the iron and manganese by digestion with potash. If to the alkaline filtrate acetic acid be then added, the phosphoric acid will be precipitated as aluminium phosphate ($Al_2P_2O_8$), and from the solution we may obtain the remainder of the alumina by precipitation with ammonia. The whole residue insoluble in potash may be estimated as ferric oxide, as the determination of manganese is of but little importance. Iron exists in coals principally as pyrites. In the filtrate from the iron, lime may be precipitated by oxalic acid, and afterwards the magnesium with sodium phosphate. To estimate the alkalis, it is, perhaps, best to weigh the residue freed from ammonia salts by ignition, as magnesium sulphate and alkaline sulphates to determine the sul-

phuric acid and magnesium present, and then to reckon the difference as alkalis.

III. *Estimation of Carbon and Hydrogen.*—5 grams of coal, after having been completely dried at 120°, and again weighed, are ignited with cupric oxide, finally in a current of oxygen, or with lead chromate, as in ordinary organic analysis, and the C and O estimated from the $CO_2$ and $H_2O$ obtained.

IV. *Estimation of Nitrogen.*—1 gram of powdered coal is ignited with soda-lime, the nitrogen evolved by ammonia absorbed by acids. The author continues to use hydrochloric acid as the absorbent, without converting the sal-ammoniac obtained into ammonium platinochloride. He merely evaporates the acid solution gradually, at a temperature not exceeding 100°. The volumetric method is not suitable in the present analysis, as in the case of a minimum of ammonia, the quantity of acid is so great as to prevent the estimation from being sufficiently accurate.

To complete the analysis of coal, the only further desirable determination would be the number of thermal units evolved by the ignition of the specimen—a thermal unit meaning the quantity of heat necessary to raise 1 gram of water 1° C.

1 gram carbon on ignition evolves 8080 thermal units.
1 gram hydrogen „ 34462 „

The thermal units desired may be obtained:—

(1.) By taking the percentage of 8080, which expresses the quantity of carbon present.

(2.) By taking the percentage of 34462, which expresses the quantity of free hydrogen present, adding the results. If for example, in a specimen analysed were found—C = 51·70, H = 3·49, and O = 10·32, the 10·32 of O would require 1·29 H for the formation of $H_2O$; there would therefore remain C = 51·70 and H = 2·20. Hence—

$$\begin{array}{lrl} (1.)\ \cdot5170 \times 8080 & = & 4177\cdot3600 \\ (2.)\ \cdot0220 \times 34462 & = & 758\cdot1640 \\ \hline \text{Total} & = & 4935\cdot5240 \end{array}$$

which expresses the number of thermal units produced by ignition of 1 gram of the specimen.

D. B.

## New Method of Alcoholometry. By E. Maumené (Compt. rend., lxxxiii, 67—70).

The author modifies Gay-Lussac's method of estimating alcohol as follows:—He distils to one-half 200 c.c. of the spirituous liquid (containing not more than 15 per cent. of alcohol), measured at 15°, and rendered slightly alkaline with caustic soda. The alcohol in the distillate at 15° is determined by a good centigrade alcoholometer, the degrees of which are referred to a special table, calculated by the author. If the distillate should contain an appreciable quantity of

ammonia, it is neutralised with a few drops of sulphuric acid, and redistilled. Alcohol may thus be estimated to within ·05 per cent.

J. R.

## Behaviour of Cellulose with the Alkaline Earths.

By H. WEISKE (Landw. Versuchs. Stat., xix, 155—159).

THE author corroborates A. Muller's statement (*J. f. prakt. Chemie*, vol. lxxxiii, page 384), that filter-paper possesses the property of precipitating from baryta-water not inconsiderable quantities of baryta. He also finds that it behaves in a similar way with strontia and lime, so that in quantitative determinations their solutions should not be filtered.

H. H. B. S.

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## Researches on the Commercial Analyses of Unrefined Sugars.

By A. RICHE and CH. BARDY (Compt. rend., lxxxii, 1438—1441).

FOR some months the mode of levying of duties in France on sugars by chemical analysis has been disputed, through some differences with regard to the quantities of the sugar employed in various laboratories, and more especially in those belonging to the government. These differences, however, are of but little importance, but the large numbers of analyses made by the authors during the last year showed that the ordinary method had some defects, and therefore required modification. In the present method the analyst is satisfied with mixing the samples by the hand and taking 16·19 grams for the saccharimeter test and 4 grams for the determination of the mineral substances. Since unrefined sugars are in the form of wet syrupy crystals, each of these samples taken may differ from others or the entire bulk of the sample. This defect may be remedied by dissolving 80·95 grams of the sugar, representing five times the quantity necessary for the saccharimeter, in 160—180 grams of cold water, and leaving the liquid at rest; then pouring it into a vessel measuring 250 c.c., the volume being made up to 250 c.c. with the washings of the first vessel. After a quarter of an hour 50 c.c. of the solution are transferred by a graduated pipette to a 100 c.c. flask and the usual saccharimetric test applied.

(1.) *Determination of the Sugar.*—The tubes employed are those constructed by Laurent, in which the glasses which close the tube are never compressed, whatever force may be used in screwing, or in whatever position the tube may be placed.

(2.) *Determination of the Saline Substances.*—The rest of the liquor is operated upon.

*a. The Liquid is quite Transparent.*—In this case, which is the most frequent of all, 10 c.c. are measured into a tared platinum capsule and about 1 c.c. of sulphuric acid added. The capsule and contents are then treated as usual.

*b. The Liquid is Turbid and charged with Suspended Matter.*—100 c.c. are filtered rapidly (the funnel being covered to avoid evaporation). The first portions of the filtrate are rejected. The pipettes in use are

provided with a glass tap, thus allowing very accurate measurements. The ashes obtained agree perfectly well with one another, while with the old method two or three milligrams were lost, which gave a very sensible difference when the weight of the analysed ash was multiplied by five.

Another error observed in the ordinary method is the presence of lime in sugar. In order to recognise this impurity, carbonic acid is passed into a portion of the solution, when a precipitate forms if lime is present. In such a case it is determined with ammonium oxalate, an excess of which does not affect polarised light.

It is unnecessary to notice the influence which salts exercise on the polarimeter, as is shown by comparative tests made with pure sugar and with the same sugar with additions of salts:

| | Deflection of the polarimeter. |
|---|---|
| Pure sugar ..... | 98·25° — 98·20° |
| ,, with potassium nitrate .. | 98·10° — 98·20° |
| ,, ,, potassium sulphate.. | 98·30° — 98·20° |
| ,, ,, potassium chloride.. | 98·00° — 98·30° |
| ,, ,, potassium carbonate. | 98·00° — 98·20° |
| ,, ,, sodium chloride .... | 98·28° — 98·40° |

D. B.

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## Volumetric Determination of Formic Acid.

By PORTES and RUYSSEN (Compt. rend., lxxxii, 1504—1505).

THE quantitative determination of formic acid in acetic acid is of some importance in solving the problem of the determination of wood-spirit in alcohol. Since formic acid reduces mercuric chloride in excess to mercurous chloride, the authors were led to utilise Personne's method, by which a given quantity of sublimate is determined with potassium iodide before and after its reduction with a certain quantity of formic acid. As the reaction is somewhat slow and not complete, it suffices to add to the solution sodium acetate, which will greatly facilitate the manipulation. 5 grams of sodium acetate are put in a retort with 25 c.c. of the solution to be determined (10 per cent. solution), and 200 c.c. of sublimate (4·5 per cent. = 9 grams) added. The mixture is heated for an hour and a half on a water-bath, until the supernatant liquid is perfectly clear; its volume is then made up to 500 c.c., and the solution filtered. By means of a graduated burette it is ascertained how many c.c. of the reduced solution will saturate one gram of potassium iodide. By a very simple calculation we obtain numbers for which a correction must be made, as shown by comparative experiments.

D. B.

## Testing of Salicylic Acid. By H. KOLBE

(J. pr. Chem. [2], xiv, 143).

DISSOLVE half a gram in about ten times that quantity of strong alcohol, pour the clear liquid into a watch glass and allow it to evaporate slowly

at the ordinary temperature. The acid will form groups of fine efflorescent crystals round the edge of the glass. These crystals should be of a pure white colour if the acid was previously crystalline, but more or less yellow if precipitated. If the crystals are at all brown the acid is impure.

G. T. A.

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**Estimation of Quinine.** By A. H. ALLEN (Pharm. J. Trans. [3], vi, 964—967).

12—15 c.c. of the quinine solution, concentrated to that bulk if necessary, are placed in a stoppered litre flask, and to it is added an excess of ammonia solution, then an equal volume of ether; after agitation and withdrawal of the ether by a pipette, ether is again added. The ethereal solution, on evaporation, leaves the alkaloïd in a weighable state. The quinine thus obtained is proved by analyses quoted to be not a trihydrate, but to contain one per cent. less water than corresponds with the monohydrate ($C_{20}H_{24}N_2O_2 + H_2O$). Soda may be employed instead of ammonia, and the results are not affected by the presence of cane-sugar, but they are somewhat in excess of the truth if the substance analysed contains foreign matter soluble in ether. This process is intended for determining the total alkaloïd present, rather than that of the actual quinine as distinguished from other cinchona bases.

E. W. P.

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**Determination of Quinine in presence of certain other Substances, and especially in Ferro-quinic Citrate.** By A. N. PALMER (Pharm. J. Trans. [3], vii, 89—91).

THE author has made experiments with the view of satisfying himself upon some points in the determination of quinine, whether, after precipitating with an alkali, the presence of glycerin, sugar, ammonium citrate, &c., interferes with the results obtained by the ether or chloroform method, and whether, by using a considerable excess of alkali, which becomes necessary in some cases, all the quinine is got out which exists in the fluid operated upon. The quinine residue left on evaporating the ethereal or chloroformic solution had to be dried at 260—270° F. and weighed before a constant weight could be obtained. (The author does not agree with Mr. Allen, who states that "ether residue" is always hydrated to the extent of 4·28 per cent.) In all the experiments, specially prepared and quite pure sulphate of quinine, and well-washed ether or chloroform were alone used. The following are the results found:—

(1.) Whether the precipitant be ammonia, potash, or soda, whether added in slight or large excess, whether the quinine solvent be ether or chloroform, is quite indifferent: in all cases the actual quantity of quinine present in the examining fluid is obtained.

(2.) The presence of sugar or glycerin does not affect the accuracy of the chloroform method, when the residue is heated to 260—270° until constant in weight. Mr. Allen has shown that sugar does not interfere with the ether process; the same may be said of glycerin.

(3.) No loss of quinine is found when it is determined in presence of ammonium citrate, so long as chloroform is the solvent employed. An ethereal layer contains only a portion of the quinine present, the remainder being held entangled in the aqueous layer, from which it can be extracted by shaking the latter with chloroform. Since the aqueous layer often tastes very bitter, and smells strongly ethereal, the author is inclined to think that the ethereal solution is rather mechanically entangled in the aqueous solution, than that the quinine is chemically retained by it.

"Ferri et Quiniæ Citras" cannot be determined by the ether method, as it contains ammonium citrate. Chloroform must therefore be employed. After the precipitated quinine has been shaken up with chloroform, the latter can be drawn off in half-an-hour. The addition of ammonia to strong rather than faint alkalinity is rendered necessary by the following fact. By adding from a burette dilute ammonia to an aqueous solution of the citrate the latter becomes distinctly alkaline to red litmus paper; it will, however, be noticed that further additions (often more than twice the first volume) of ammonia give a further precipitate of quinine. Four samples of quinine from different makers gave by this method 14, 14·4, 14·2, and 15·37 per cent. respectively of the pure dry alkaloïd. The method is absolutely trustworthy, as it is simple in application, and rapid in execution.

D. B.

**Rhodeine from an Analytical Point of View.** By E. JACQUEMIN (Compt. rend., lxxxiii, 448—449).

THIS body, which has a magnificent rose colour, is produced by the successive action of a hypochlorite and a sulphide on aniline, even when minute traces only of that base are present. The author, in a former paper on erythrophenic acid, showed that if, on addition of traces of aniline to a liquid, a blue coloration was produced by the action of sodium hypochlorite, the presence of phenol might be inferred. He has since found reason to modify this conclusion, and now gives the following process for the detection of phenol.

When a drop of pure aniline is added to a certain volume of alcohol diluted with water, and then sodium hypochlorite, the fugitive violet colour usual in aqueous solutions is not produced, but instead of it a yellowish coloration, passing quickly into green, and then into a permanent blue-green. This reaction is not absolutely decisive, but the following test places the matter beyond doubt.

The bluish-green liquid is diluted after some time with an equal volume of water, and a few drops of a very dilute solution of ammonium sulphide are added, so as to obtain, if aniline alone has produced the colour, a rose-purple coloration of rhodeine, which fades and leaves a yellow liquid; whereas, if the reaction was produced by aniline and phenol, and the erythrophenate of sodium was well developed, the addition of sulphide would restore the blue in all its purity, only to turn it into a yellow liquid as before. To distinguish these two yellow liquids, it is sufficient to add sodium hypochlorite, which in one case gives the fugitive violet of aniline, becoming brownish in twenty-four

hours, and in the other re-establishes the erythrophenate blue, which does not fade.

H. W.

## The Quantitative Estimation of Albumin in Blood-serum and Milk. By J. Kuls (Pflüger's Archiv., xiii, 176—196).

Comparative experiments were made on the best method of determining albumin in blood serum and milk. Preference is given to precipitation by alcohol, after neutralisation with acetic acid and warming. The percentage of alcohol required in the liquid need not exceed 70 per cent.; less, even 63 per cent., will do, but the filtration is then more difficult.

Incidentally an analysis of human milk is given, and the percentages are given as albuminoïds 0·97, fat 3·08, and sugar 5·26 per cent.

T. S.

## Optical Behaviour of Wines, &c. By C. Neubauer (Zeitschr. Anal. Chem., 1876, 188—220).

In the first part of this paper it is shown that commercial grape-sugar contains considerable quantities (16, 20, 24 per cent.) of an unfermentable body. This substance is partly soluble, partly insoluble in alcohol; it is not sweet, nor does its concentrated solution deposit dextrin on addition of alcohol. This substance is neither gum nor sugar, but it may be transformed into sugar by long-continued boiling with dilute sulphuric acid. The substance is non-crystalline: it very slightly reduces Fehling's copper-solution. That portion which is soluble in alcohol showed a specific right-handed rotation of 78°, and a rotation constant of 1282°: the insoluble portion showed 93·52° and 1069·3° respectively.

The preparation of chemically pure grape-sugar is discussed, preference being given to the method of Schwarz somewhat modified.

It is then shown that ordinary wines exert no rotatory action on the polarised ray when fermentation has ceased, but that very fine (German) wines—Johannisberg, Rüdesheimer, &c.—cause the ray to rotate to the left: hence, if it be found that a sample of wine causes right-handed rotation we may conclude that this sample is adulterated with commercial grape-sugar. Various experiments are detailed in support of this proposition. The author recommends the polaristrobometer of Wild: if the wine be dark-coloured, it must be treated with animal charcoal. In some cases it is necessary to evaporate 100—500 c.c. to a small bulk, drain off from crystals, and decolorise before using the polaristrobometer. The amount of dextro-rotatory action in the samples of spurious wines examined by the author varied from 0·8° to 7·9°, using a tube 200 mm. in length.

Experiments are also detailed which were made to determine whether or not, at certain periods, grape-wort contains cane sugar in addition to lævulose and dextrose, and also whether the last-named sugars are always present in that proportion in which they are found in inverted sugar.

These experiments are not yet, however, so complete as to permit of just conclusions being deduced.

M. M. P. M.

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**Detection of Fuchsine in Wine.** By E. JACQUEMIN (Compt. rend., lxxxiii, 70—73).

FUCHSINE or rosaniline used to colour wines may be detected by the following methods.

1. A small quantity of gun-cotton is heated for a few minutes in 10—20 c.c. of the wine to be tested, and then washed with water. The colour thereby communicated to the gun-cotton by rosaniline, if present, resembles that of archil, which is also used to colour wines. The two colouring matters may, however, be readily distinguished by means of ammonia, which turns archil violet, but decolorises rosaniline.

2. The wine (100 c.c.) is first heated till alcohol is nearly expelled, a thread of white embroidery wool, previously wetted, is then immersed in it, and the liquid is slowly boiled down to half its bulk. If fuchsine is present, the wool retains, after washing, the colour of that substance. Archil dyes wool a similar colour, but the two colouring matters are readily distinguished by the behaviour of the dyed wool with ammonia.

3. A quantity of the wine (100—200 c.c.) is heated in an open vessel till alcohol is almost completely driven off, then allowed to cool, mixed with excess of ammonia, and finally shaken with ether, which dissolves ammoniacal fuchsine, if present. On evaporating the ethereal solution, white wool immersed in it acquires the characteristic colour of fuchsine.

J. R.

**Detection and Estimation of Fuchsine and Arsenic in Wines which have been artificially coloured with Fuchsine.** By C. HUSSON (Compt. rend., lxxxiii, 199—201).

FOR detecting the fuchsine the following process is given. Place a few grams of the wine in a phial and add ammonia; into the mixture dip a piece of white Berlin wool, and when it is well soaked, withdraw it, and allow a drop of vinegar or acetic acid to run down it. The wool becomes quite white if the wine is pure, but is tinted red if fuchsine is present, the depth of the colour being proportional to the quantity of fuchsine.

It was found by experiment upon a rabbit that pure fuchsine is not of itself a violent poison, although it produces some toxic effects.

The method of estimating the arsenic which may have been introduced with the fuchsine into the wine, depends upon the fact that if arseniuretted hydrogen be passed into a solution of iodine in benzene, the colour of that solution is rapidly destroyed, whilst it is not affected by pure hydrogen.

It was found by experiment that 0·01 gram of arsenic in the form of arseniuretted hydrogen was decomposed by 0·02 gram of iodine. The process is to be practised as follows:—

Having decomposed the suspected matter by the ordinary processes, so as to obtain the arsenic as a potash-salt, this is dissolved in distilled water, and the solution divided into two parts; one is reserved for qualitative examination, the other divided into two, in one of which the arsenic is approximately determined by pouring it into a Marsh's apparatus which is evolving pure hydrogen, and passing the gas into a measured quantity of a standard solution of iodine in benzene, and as this is decolorised, gradually adding more from a burette until the decolorisation ceases. In the other part of the solution the quantity of arsenic is exactly determined by pouring it into a Marsh's apparatus as before, and allowing the evolved gas to pass through a series of about six test-tubes, each containing a known amount of iodine: for example, in the 1st 0·01 gram; 2nd and 3rd, 0·005 gram; 4th, 0·001 gram; 5th, 0·0005 gram; and 6th, 0·0001; but these quantities may be varied according to the indications afforded by the previous experiment. By noting the number of test-tubes coloured, the exact quantity of arsenic introduced into the Marsh's apparatus can be ascertained.

C. H. P.

## Detection of Artificial Colouring Matter in Wines.

By L. LAMATTINA (Compt. rend., lxxxiii, 564—565).

THE usual colouring matter is fuchsine. It may be detected by mixing 100 grams of the wine with 15 grams of coarsely powdered manganese dioxide, shaking for 12 or 15 minutes, and filtering through a double filter-paper. If the wine is pure it passes through colourless; if adulterated, some artificial colouring matter has been used. If pure peroxide is used, this process is unexceptionable; but if the manganese contains iron the acids of the wine dissolve it, and it forms an insoluble lake with the colours which remain on the filter. If in this case the residue on the filter is treated with alcohol, the fuchsine dissolves, and may be immediately recognised by adding strong acetic acid and a few drops of ammonia.

W. R.

## Estimation of the total Nitrogen in Urine.

By W. P. WASHBURNE (Bull. Soc. Chim. [2], xxv, 498).

EVAPORATE 5 c.c. of the urine to dryness on 10 grams of plaster of Paris, mixed with 0·5 gram of oxalic acid. There is no difficulty in subsequently detaching the plaster from the basin. Mix the plaster with soda-lime, and burn it in a combustion tube as in the ordinary method of determining nitrogen in organic bodies. The results are accurate.

C. H. P.

**How long after Death do the Evidences of Phosphorus-poisoning remain in the Body?** By FISCHER and MÜLLER (Zeitsch. Anal. Chemie., 1876, 57—60).

FOUR Guinea pigs were poisoned with equal doses of phosphorus. The phosphorus for this purpose was derived from the heads of lucifer matches, and, according to an accurate determination, each animal received 0·023 gram. Within a few hours all four died, and they were then buried at a depth of half a meter in a sandy soil.

At the expiration of four weeks the first was dug up, and examined by Mitscherlich's method of distillation, when the presence of unoxidised phosphorus was clearly shown.

At the expiration of eight weeks the second was disinterred and examined, with a similar result.

The third was allowed to remain twelve weeks in the ground, at the end of which time no trace of free phosphorus could be detected, although there was distinct evidence of the presence of phosphorous acid.

After the lapse of fifteen weeks the fourth was examined, but no trace of either free phosphorus or phosphorous acid could be detected. The whole of the phosphorus had undergone complete oxidation.

The chief result arrived at by these experiments, viz., that the evidences of phosphorus poisoning are recognisable in the corpse with positive certainty after twelve weeks' interment, does not completely agree with that observed in the case of human beings; but in the first place the dose for such small animals was moderately large; then death occurred without that vomiting which in the case of human beings generally causes the ejection of more or less of the phosphorus; and, lastly, the hide of the Guinea pig would certainly resist the passage of air to a greater extent than the skin of a human being; nevertheless the experiments show that the phosphorus remained in the corpse for a longer time than, judging from its rapidity of oxidation, would have been expected.

H. H. B. S.

## Technical Chemistry.

**On the Manufacture of Chlorine by Deacon's Process.** By R. HASENCLEVER (Deut. Chem. Ges. Ber., ix, 1070—1073).

IN working Deacon's process on the manufacturing scale, it is found that the yield of chlorine, which is abundant at first, becomes after a time less and less, until it is reduced almost to nothing. This circumstance appears to be due to absorption by the clay balls of the sulphuric acid always present in the gases operated on. The author examined some clay balls which had ceased to act, and found in them 1·2 per cent. of copper and 8·0 per cent. of sulphuric anhydride, whereas balls freshly saturated with cupric sulphate contained 1·2 per cent. of copper and the corresponding quantity only, namely 1·5 per cent., of sulphuric anhydride.

In the manufacture of sodium sulphate the hydrogen chloride set free is evolved partly from the pans in which the sulphuric acid and salt are first mixed, and partly from the ovens in which the mixture is afterwards heated, the gas from the ovens always containing much more sulphuric acid than that from the pans. Now it is found in practice that in those factories where the gas from the pans alone is used for the preparation of chlorine by Deacon's method, the process goes on for many months with the same decomposing materials, but where the gas from the ovens is also used, the activity of the materials ceases much sooner. These facts seem to favour the foregoing suggestion. The author proposes to absorb the sulphuric acid, and to use the purified gas for the preparation of chlorine.

J. R.

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## Manufacture of Soda from Salt.

(Dingl. polyt. J., ccxxi, 93).

H. GRÜNEBERG and J. Vorster propose the following method:—Salt and alumina are mixed with water to a pulp, and the mass is dried, broken into small pieces, and treated with steam heated to dryness. Hydrochloric acid then escapes, and sodium aluminate remains behind, the latter is freed from admixtures by lixiviation, and either decomposed by means of carbonic acid or with caustic lime.

Instead of alumina, ferric oxide or any other metallic oxide may be used. If caustic potash is to be prepared, the common salt is replaced by potassium chloride.

D. B.

## Recovery of Sulphur from Gypsum and Glauber's Salt in the Manufacture of Glass. By O. SCHOTT (Dingl. polyt. J., ccxxi, 142—146).

THE injurious action which sulphurous acid escaping in considerable quantities from glass-works has on vegetation, induced the author to try some experiments with the view of rendering this gas less active and injurious, by collecting and recovering it. It was shown (1875, ccxv, 533), that Glauber's salt, if treated with coal and silicic acid, is decomposed into $SO_2$, $CO_2$ and sodium silicate, but the reason why this reaction was not used in practice for recovering sulphurous acid must be found in technical difficulties accompanying it. Sodium silicate strongly attacks the sides of the oven in which it is fused, and the cost of fuel, labour, &c., is too large to be covered by the yield of acid obtained. A silicate of sodium and calcium obtained by mixing Glauber's salt, gypsum, coal, and silicic acid was found to give more favourable results, as less heat was needed, and the presence of calcium silicate did not affect the apparatus so much, as it caused, to some extent, a neutralisation of the sodium silicate with an earth. A glass mixture, in which the lime was added in the form of gypsum, with a larger quantity of coal, showed that calcium sulphate might be easily fused with glass. By the addition of gypsum in place of the carbonate, it is seen that a second problem, viz., preparation of sulphur

from gypsum, would thus be solved, which might become of some importance to acid manufacturers.

The mixture of gases evolved was found to consist of 2 vols. of $SO_2$ and 1 vol. of $CO_2$—a proportion which the author thinks to agree with that of the mixture of gases evolved when pyrites are burnt, the carbonic acid of the former behaving as indifferently as the nitrogen which is always present in the latter.

In conclusion a calculation is given, which seems to show, that by separating the sulphur from Glauber's salt and gypsum, and collecting the gas mixture in chambers, the yield of the new product obtained would be sufficiently large to cover two-thirds of the total production of the sulphate in England, not taking into account the advantages which this method would offer to the neighbourhood of glass-works.

D. B.

## Chinese Porcelain Manufacture. By A. Heintz (Dingl. polyt. J., ccxxi, 156—166).

In the first part of the paper, a history of the porcelain manufacture in China is given, after which the author goes on to a description of the raw materials and the several manipulations of the Chinese porcelain manufacture.

*Kaolin* has its name from a felspar mountain situated near Kingletschin, porcelain earth having been formed by its decomposition. Salvètat analysed some samples which were sent to Paris from China. I is a sample of washed clay from Tongkong. II. From Sikang. *a* and *b* are kaolins from St. Prieix, near Limoges, their composition being very similar to Nos. I and II. The latter are porcelain clays originating from pegmatite, which are used in Sèvres :—

| | I. | *a.* | II. | *b.* |
|---|---|---|---|---|
| Loss by ignition .... | 11·2 | 12·62 | 8·2 | 7·2 |
| Silicic acid..... | 50·5 | 48·37 | 55·3 | 56·9 |
| Alumina..... | 33·7 | 34·95 | 30·3 | 31·6 |
| Ferric oxide ..... | 1·8 | 1·26 | 2·0 | 0·5 |
| Lime ..... | 0 | 0 | 0 | 0·5 |
| Magnesia ..... | 0·8 | traces | 0·4 | 0 |
| Potash ..... | 1·9 | 2·4 | 1·1 | 3·4 |
| Soda ..... | 0 | | 2·7 | |

Chinese porcelain earth contains, in its natural state, undecomposed portions of felspar, quartz, mica, and occasionally iron pyrites, from which it is separated by washing with water, sifting, drying, putting the mass into a large cloth, pressing it, and forming it into squares.

*Felspars* are treated in the same manner as kaolin. The rock is broken up with pickaxe and hammer, and powdered in large mortars or in crushing-mills. The finer portions are washed and formed into "white briquettes," and the coarser powder is again brought into the mill. The following samples were analysed by Salvètat. 1, 3, 5, 7, 10 are crude felspars. 2, 4, 6, 8, 9, 11 are finely powdered and washed. 12 is a sample of pegmatite from St. Prieix :—

| | 1. | 2. | 3. | 4. | 5. | 6. |
|---|---|---|---|---|---|---|
| Loss by ignition .... | 2·94 | 3·05 | 3·10 | 3·05 | 3·76 | 3·25 |
| Silicic acid..... | 76·20 | 76·26 | 74·90 | 75·00 | 76·30 | 76·41 |
| Alumina..... | 13·60 | 14·20 | 14·00 | 14·15 | 13·15 | 13·90 |
| Ferric oxide ..... | traces | traces | 0·80 | 0·10 | 0·85 | 0·90 |
| Manganic oxide..... | ,, | 0·35 | 0·20 | traces | 0·30 | traces |
| Lime ..... | 0·12 | traces | traces | 0·12 | traces | 0·35 |
| Magnesia ..... | traces | ,, | ,, | 0·15 | ,, | traces |
| Potash ..... | 3·28 | 3·00 | 3·00 | 3·10 | 3·10 | 3·00 |
| Soda ..... | 5·05 | 4·00 | 3·90 | 3·04 | 2·17 | 2·50 |

| | 7. | 8. | 9. | 10. | 11. | 12. |
|---|---|---|---|---|---|---|
| Loss by ignition .... | 2·4 | 2·4 | 2·6 | 2·0 | 2·5 | 0·40 |
| Silicic acid ..... | 74·7 | 77·0 | 74·4 | 75·4 | 73·6 | 76·10 |
| Alumina ..... | 15·9 | 15·7 | 15·0 | 16·0 | 17·8 | 15·37 |
| Ferric oxide ..... | — | — | traces | 0·1 | — | 0·13 |
| Manganic oxide .... | 0·1 | — | — | traces | traces | — |
| Lime ..... | 0·1 | 0·2 | 0·1 | 0·4 | 0·5 | 0·17 |
| Magnesia ..... | 0·2 | — | — | traces | 0·1 | traces |
| Potash ..... / Soda ..... | 6·4 | 4·7 | 6·9 | 6·0 | 5·5 | 2·84 / 4·58 |

The mixing of felspar with porcelain clay is effected by crushing briquettes of the two substances in large mortars, washing the powder with water, and decanting the latter. The proportions of mixing vary considerably. For fine porcelain, equal parts of the raw materials are mixed; for inferior qualities, an excess of felspar is used generally. Salvètat, however, could not quite confirm this assumption by analyses, but he found that the smallest proportion of iron was contained in the finer porcelains. The mass is rendered suitable for forming, after being left to disintegrate for a long time, sometimes 100 years, by very careful kneading, treading, and beating. The forming operations in China are the same as those used in Europe. Their method, however, differs very essentially from the European method by the fact, that in China the porcelain mass is not heated before the glazing operation. Chinese porcelain is more readily fusible than the European material: and the same observation applies to the substances used for glazing. The following gives the composition of two burnt glazing masses:—

| | | |
|---|---|---|
| Silicic acid..... | 68·0 | 64·1 |
| Alumina..... | 12·2 | 10·2 |
| Ferric oxide ..... | traces | traces |
| Lime ..... | 14·0 | 21·0 |
| Alkali..... | 6·0 | 5·1 |

A compact limestone is covered alternately with a thin layer of ferns and burnt, the product extracted with water, and after the addition of gypsum purified by repeated washing. After the lime water has been mixed with fine felspar to a thin slime, it is ready for use.

The painting of porcelain articles must be effected before the

glazing operation takes place. For this, manganese ores containing cobalt, or preparations of cobalt, are used. The ores are sorted out according to external appearances, then ignited, broken up into small pieces, washed with water, and powdered whilst moist, A sample of blue ore from Yünnan contained, according to Salvètat's analysis:

| | |
|---|---|
| Silicic acid and insoluble residue | 37·46 |
| Cupric oxide | 0·44 |
| Alumina | 4·75 |
| Cobaltic oxide | 5·50 |
| Manganic „ | 27·50 |
| Ferric „ | 1·65 |
| Lime | 0·60 |
| Magnesia, arsenic, nickel | traces |
| Loss by ignition | 20·00 |

The minerals designated as Hoachy are partly impure fatty clays, used for pâte-sur-pâte work, partly rocks rich in magnesia, which, when added to the glazing substances, yield articles covered with a dense net of small cracks. The furnaces used for burning are 3·15 m. high, 3·15 m. wide, 6·30 m. long, with a chimney 6·30 m. high. The time required for burning is said to be from 8 to 3 days. Besides the blue colour above-mentioned, various other colours are used for decorating purposes; the following are the principal colours and their composition:—

| | |
|---|---|
| Ivory white | Lead oxide, silica, and arsenic. |
| Black | Manganese, cobalt, oxide of copper and of lead. |
| Blue | Fluor spar (1) with cobalt; (2) with copper. |
| Yellow | Antimony. |
| Green | Antimony and copper. |
| Red | Ferric and lead oxide, fluor spar. |
| Carmine | Fluor spar with gold. |
| Pink | Lead oxide, silica, arsenic, felspar and gold. |

D. B.

## Formation of Boiler Incrustations.

(Dingl. polyt. J., ccxxi, 89—90).

H. Hanisch has analysed a boiler-deposit of the following composition:—

| $H_2O$. | CaO. | $SO_3$. | MgO. | $CO_2$. | $SiO_2$. | $Al_2O_3$ and $Fe_2O_3$. | $P_2O_5$. | Insoluble. |
|---|---|---|---|---|---|---|---|---|
| 9·43 | 32·66 | 47·70 | 2·93 | 2·43 | 0·60 | 2·50 | 0·82 | 0·45 = 99·52 |

After the application of De Haën's method, a thin but hard deposit was obtained, which consisted of—

| BaO. | $SO_3$. | MgO. | Cl. | CaO. | $H_2O$. |
|---|---|---|---|---|---|
| 54·98 | 32·70 | 7·35 | 0·11 | trace | 4·22 = 99·36 |

Hanisch is of opinion that the conversion of part of the barium chloride by the sulphates at 56°, does not take place in the clarifying vessels, but in the boiler itself, and that thus the separated barium sulphate forms a solid crust with the magnesium hydrate.

D. B.

## Use of Calcium Chloride for Watering the Roads of Streets and Parks. By A. Houzeau (Compt. rend., lxxxii, 1507—1509).

The author mentions that calcium chloride is largely employed for watering the streets of Rouen, where the waste products from the pyroligneous acid manufacture are utilised. Calcium chloride impregnates the soil with hygrometric matter, and thus keeps it moist for a whole week. The chloride obtained from the manufacture of pyroligneous acid always contains notable quantities of iron chloride and tarry matter, whose volatilisation into the air is sure to be conducive to health. It also represents a saving of 30 per cent. on the watering with water alone. For instance in the very hot season a road one kilometer long and five meters wide requires four waterings per day. The total water used is 16 cm. per day, the cost of which is 10 francs (including horse and driver). The same road consumes only four cubic meters of the chloride solution 33° B., costing 7·50 francs per cm. (one cm. of 20° B. chloride solution costs 4·50 francs), but the effects of the humectation last for six days, during which time all watering may be suspended.

Thus it seems that the use of calcium chloride is very advantageous, as it not only removes the above-mentioned difficulties, but also forms a kind of hard incrustation on the soil, which is about 1—2 mm. thick and resists for some days not merely the desiccation of the soil but also prevents the disaggregation caused by the traffic of vehicles, &c. When used for watering avenues in parks, it hinders the growth of grass and thereby economises labour.

D. B.

## Wearing out of Platinum Vessels in the Concentration of Sulphuric Acid. By A. Scheurer-Kestner (Dingl. polyt. J., ccxxi, 82—84).

The action of sulphuric acid on platinum varies according to the purity, and especially the concentration of the acid. The presence of nitrogen doubles or trebles the loss of metal, and in preparing sulphuric monohydrate a much greater loss is occasioned. Some experiments were made by the author so as to answer the question whether the loss of platinum takes place mechanically or whether the metal is dissolved. It was found that the loss of platinum per ton of concentrated sulphuric acid of 66° (containing 93—94 per cent. monohydrate) amounted to 2·859 grams. The acid, however, contained nitrogen. When this was removed with ammonium sulphate, the loss was 1·220 grams. The presence of sulphurous acid in the sulphuric acid occasioned a loss of 0·925 grams per ton of concentrated acid. Hydrochloric acid did not

materially alter the solution of the metal. While the loss in concentrating acid of 66° B. amounted to about one gram per ton, the loss was much higher when an acid containing 97—98 per cent. of monohydrate was produced, viz., 6 grams per ton. The above mentioned numbers give only the quantities of metal dissolved in the boiler itself, not noticing the other parts of the platinum vessel. It was shown that, in order to give the total loss of platinum, about 13 per cent. must be added to the above mentioned numbers. From the results obtained it follows:

(1.) The loss of platinum in the boilers does not originate from a simple mechanical action of the boiling acid.

(2.) Sulphuric acid free from nitrogen dissolves about one gram of metal per ton of concentrated acid when acid of 94 per cent. monohydrate is produced. The loss amounts to 6—7 grams when acid is produced containing 98 per cent., and to 9 grams when it is produced with 99½ per cent. of monohydrate. Acid containing nitrogen attacks platinum more strongly. Platinum containing iridium resists the action of acid much better than pure platinum, but it cannot be used in practice as it is much more brittle than the former. Two platinum capsules, one made of pure platinum and the other of platinum alloyed with 30 per cent. of iridium, were left in a platinum still for 57 days. The loss of weight of the platinum capsule was 19·66 per cent., that of the platinum iridium capsule only 8·88 per cent.

D. B.

## The Present State of the Rice-starch Manufacture.

By M. Adlung (Dingl. polyt. J., ccxxi, 58—63).

Rice-granules contain more than 80 per cent. of starch, a quantity which surpasses that contained in all other raw materials suitable for the preparation of starch. Since rice-starch, on account of the smallness of its granules, possesses a greater fineness, and on application a much higher lustre than wheat-starch, its preparation may be regarded as a remunerative business in places where rice can be got cheaply. It is true that the rice-starch manufacture is attended with difficulties different from those which occur in the preparation of starch from potatoes or wheat; the amylum granules are enclosed in firm cellular tissues, and joined to one another by a small but very resisting quantity of gluten, so intimately that their separation can be effected only by the aid of chemical agents, alkalis or acids.

In order to prepare rice-starch successfully, we must in the first place have a sufficiency of a clear water free from organic matter and iron. A large proportion of sulphates, calcium, and especially magnesium chloride is always disadvantageous, from the fact that such salts decompose part of the caustic alkali employed in the process, and also because caustic magnesia hinders very much the separation of the so-called gluten-starch from the fine starch. Sodium chloride, however, if alone present in water favours this separation. In the second place liquors of a certain concentration should be used, and the whole apparatus should be in good condition. Caustic soda forms at present the only solvent for gluten. The author distinguishes three methods of treating the product when separated:

I. An English method according to O. Jones.

II. An Anglo-German method, E. Hoffmann and others.

III. An American method (which he intends to describe in a further communication).

The above-mentioned methods have in common:

(1.) The soaking of the rice in caustic soda of 1½—2° B. The liquor remains in contact with the rice for about 18 hours with constant agitation.

(2.) Two washings of the swelled rice.

(3.) Grinding with addition of 1° B. soda-lye made up to a fine but somewhat thick liquid pap. According to Jones, the pap is agitated for about five hours, pumped into large vessels placed on the second floor of the building, diluted with an equal volume of water, and allowed to stand for 20 minutes, when the greater part of the gluten, starch, and cellulose are thrown down to the bottom of the vessel. The liquid is syphoned off, and the same operation repeated three times, adding some calcined soda to the water. The milk of lime obtained passes through a cylindrical sieve into large tin-plate vessels, where the solid starch is deposited. After two days the liquid is drawn off, the solid taken out, treated with water containing a slight addition of soda, and brought into a centrifugal machine. In Hoffmann's method, the thin pulp is treated in large vessels with an equal bulk of soda-ley of 1° B., the mixture after six hours' agitation, diluted with an equal bulk of water and left at rest. After 40 minutes the liquid is drawn off, and the residue again treated with very dilute soda-ley. The further treatment of the starch is similar to that of the former method. In order to obtain starch in rays, the above solid is treated with water, neutralised with dilute hydrochloric acid, and after the addition of a small quantity of ultramarine blue, drained on linen cloths placed on wooden boxes. The solid mass is then divided into equally large lumps, which are placed on porous bricks or gypsum plates, and put into an oven to dry, when no more moisture is perceived. The temperature should be from 50—60°, and the damp air carried off by an exhauster. When the lumps have assumed a crust of 2—3 mm. thickness, they are scraped, put into paper and dried at a higher temperature. The damp air should be exhausted for about four days, after which all openings are closed and the starch is heated to 75° for about two days. The paper packets are then cooled in a dry place and the starch is ready for use. The residue left in the extracting vessels and containing fine starch, gluten starch, gluten and small pieces of rice, yields a first-class secondary starch-product. It is treated with water, and the mixture passed through a sieve. The unground rice-particles are brought back to the mills, and the liquid is exposed to fermentation, a small quantity of decomposed wheat gluten having been mixed with it. In order to remove the dissolved substances, the whole mass is passed through a centrifugal machine, the residue treated with water and a small quantity of calcined soda, the liquid drawn off, and the solid treated as above. The further treatment of the resulting starch is similar to that of wheat starch. By these methods the yield of starch (fine and secondary starch) amounts to over 65 per cent. (*Deutsche Industrie Zeitung*, 1876, p. 142, 228). D. B.

**Method of Softening Water used for Dyeing with Madder Colours.** By A. ROSENSTIEHL (Dingl. polyt. J., ccxxi, 167—169).

IT is a well known fact, that the actual yield of colouring matter is always larger than is shown by experiments on a small scale. A small quantity of water is apt to give up its carbonic acid when warmed, more readily than a large quantity of water, which generally retains its carbonic acid during the whole of the dyeing operation. It is found that alizarin requires a certain quantity of lime in the bath, to saturate the mordants completely; that purpurin does not absolutely require the same; and that with pseudopurpurin shades can be obtained only when pure distilled water is employed; that the lime lake of alizarin is readily decomposed by free carbonic acid, that of purpurin decomposed only with difficulty, and that of pseudopurpurin not decomposed at all. This fact explains the impossibility of undertaking two consecutive dyeing operations in one and the same bath, even when the right quantity of chalk has been added to the colouring matter, as the remaining carbonic acid is not sufficient to dissolve the latter and to render it active in the bath. In order to correct this defect, sodium bicarbonate was used, but the author was obliged to give up the use of this salt, on account of its instability, and to introduce a stream of carbonic acid into the bath. In this manner results were obtained which corresponded with those made on a large scale, a saving of as much as 20 p.c. of colouring matter being occasioned. At the present time Rosenstiehl recommends the use of a solution of calcium acetate, which salt is able by its acid nature to decompose the natural and also the artificial madder colours at the boiling temperature. 1 eqiv. of the acetate for 1 eqiv. of alizarin gives very good dyeing results. Purpurin also colours mordants more readily in presence of this salt, and pseudopurpurin admits an addition of the same salt even when added in excess. It has been further proved by experiments, that madder extracts and the reds and violets of artificial alizarin saturate mordants very readily and completely in presence of 2 eqiv. of acetate of lime, the bath being much clearer than is the case with carbonic acid.

Rosenstiehl uses this salt in the following manner:—The water used is that of the Doller. It contains 50 mg. (1 mg. eqiv.) of calcium carbonate in 1 litre; this salt is converted into the acetate by adding 10 c.c. of a $\frac{1}{10}$ of normal acetic acid (in the liter 6 grm. $C_2H_4O_2$ or 18·3 c.c. acetic acid of 1·045 sp. gr.). The quantity of acetate of lime present in 1 litre of the river water is therefore equivalent to 0·240 grm. of alizarin or 0·256 grm. of purpurin. To obtain the right proportion of 2 eq. of lime salt to 1 eq. of colouring matter, 10 c.c. of a $\frac{1}{10}$ solution of acetate of lime has to be added. This latter solution is obtained by mixing 41·5 grm. of a solution of lime acetate of 1·115 sp. gr. with 6·1 gr. of acetic acid of 1·045 sp. gr. and making the mixture up to one liter.

D. B.

## Alcoholic Solution of Shellac.

By A. PELTZ (Pharm. J. Trans. [3], vii, 94—95).

THE object sought by the author was to obtain a clear alcoholic solution in a short time without much loss. A previous communication upon the substance occurring in shellac to the extent of 5 p. c. which renders its alcoholic solution turbid, and described by some authors as wax or a fat-acid, suggested an attempt to effect its removal before dissolving the shellac. The author prepared a solution of 1 part of shellac and 6 parts of 90 p. c. alcohol at the ordinary temperature. To this he added magnesium carbonate to about half the weight of the shellac used, and heated the mixture to 60° C. Although the solution cleared more rapidly than one not treated with the magnesium salt, it did not supply what was sought. Powdered chalk when treated in like manner gives a solution which is three-fourths clear, whilst the lower portion could be rapidly filtered. On a large scale it would be best filtered through felt. By adding to 3 parts of the alcoholic solution 1 part of petroleum-ether, two layers were obtained, the upper light-coloured layer containing the petroleum-ether with the wax dissolved in it. By using a stronger alcohol (95 p. c.) the two layers could be separated only after the addition of water. Further experiments showed that the petroleum-ether could be replaced by ordinary commercial benzol.

D. B.

## Use of Vanadium in the Preparation of Aniline Black.

By G. WITZ (Compt. rend., lxxxiii, 348).

IT is found by experiment that for the preparation of thickened colours for printing, the quantity of vanadium should be exceedingly small in comparison with the weight of aniline salt employed. It is sufficient to take of vanadium from $\frac{1}{50000}$ to $\frac{1}{200000}$ of the weight of aniline hydrochloride, to obtain in a few days, when dyeing by impression, a sufficient oxidation. An average quantity of $\frac{1}{50000}$ of the weight of aniline hydrochloride may be adopted where 80 grams of this salt are used to form 1 liter of colour. Preparations with copper sulphate have been abandoned and replaced by vanadium, which affords quicker and better results, and has the following advantages:—

1. Improvement in the richness of the black, and clearness of the impression.
2. Avoidance of the attacking of the rollers.
3. Facility of the regulation of the duration of the oxidation.
4. Lengthened preservation of the thickened colours. (They may be kept several weeks without alteration).
5. More simple, and economical preparation than hitherto used. It is estimated that the cost for vanadium should not exceed $\frac{1}{11}$ of that for the copper usually employed.

C. H. P.

## Carbon Bisulphide as an Antiseptic. By P. ZÖLLER (Deut. Chem. Ges. Ber., ix, 1080—1084).

THE author has continued his experiments on this subject, with the object of determining (1) the minimum quantity of bisulphide required, and (2) whether articles of food preserved by means of it are fit for human consumption.

As regards the first point, he found that meat of all kinds, and even entire animals, in quantities up to 20 kilograms, kept perfectly well for several weeks in vessels of sheet-zinc, into which 5 grams of carbon bisulphide had been introduced, the meat being either simply hung on hooks or wrapped in cloths and laid on perforated shelves in the vessels. Probably a smaller quantity of the bisulphide would suffice. Meat also kept well for 62 days in a vessel in which carbon bisulphide was liberated by introducing potassium xanthate and dilute sulphuric acid. Freshly baked bread, vegetables and fruits of all kinds (asparagus, radishes, young beans, cucumbers, strawberries, raspberries, currents, cherries, peaches, apricots, lemons, &c.), and juices of fruits, kept perfectly well in glass vessels into which carbon bisulphide had been introduced in the proportion of 5—10 drops for each liter of capacity.

Bread, vegetables, and fruits thus preserved are fit to eat after simple exposure to air, and cannot be distinguished by taste or other qualities (except a slight loss of colour in some fruits) from fresh bread, &c. Meat retains, even after exposure to air, the disagreeable odour of carbon bisulphide. But besides this odour, which disappears on boiling or roasting, the meat has a slight smell of the volatile fatty acids and the taste of game. To most people, however, this taste is not unpleasant. The presence of fatty acids is to be attributed to decomposition taking place in the interior of the meat, and not preventable by the carbon bisulphide, the function of which is merely to kill germs present in the air or on the surface of substances submitted to its influence.

J. R.

## Crystallisation of Sugar. By G. FLOURENS (Compt. rend., lxxxiii, 150—152).

THE author finds that Dutrôné's tables of boiling points of solutions of cane-sugar, which are still reproduced in works relating to the sugar industry, are inaccurate. He has determined (1) the amount of sugar in saturated solutions at temperatures between 0° and 100°; (2) the readings of Beaumé's hydrometer and Gay-Lussac's densimeter in these solutions at the observed temperatures and at 15°; and (3) the boiling-points of solutions of different strengths as indicated by the hydrometer. The results are given in the form of tables.

J. R.

**Results Obtained with New Apparatus for Extracting Juice from the Sugar-cane.** By MIGNON and ROUART (Compt. rend., lxxxiii, 532—534).

THE authors have constructed a machine which serves the double purpose of removing the fibre from sugar-cane, and extracting the juice. The machinery for removing the fibre is similar to that invented by the MM. Labrousse for making paper from straw. The compressing is achieved with two hydraulic presses, one capable of withstanding 12 atmospheres, and the other about 68 atmospheres pressure. The percentage of juice obtained, referred to the unpressed cane, was 77 per cent. This yield is very much higher than that obtained by the old process.

W. R.

**Transformation of Saccharose into Glucose in the Operations of Sugar-refining.** By A. GIRARD (Compt. rend., lxxxiii, 196—198).

NOT only in the acid, but also in the neutral liquids of the sugar refinery, the author found that a considerable proportion of saccharose was converted into glucose by keeping the liquids at a temperature of 65° for a number of hours. The amount of the saccharose which disappeared was, however, not always equal to that of the glucose formed. The agent in the transformation is believed by the author to be the glucose previously existing in the crude products.

R. R.

**Manufacture of Dynamite.** By A SOMBERO (Compt. rend., lxxxiii, 350).

IT is suggested that dynamite might be made by forming a sort of cake from the fossil earth called *Kieselguhr*, from Santa Fiora, or a similar kind of porous substance, drying the cakes at 100°, and after cooling saturating them with nitroglycerin. The saturation would be effected by placing the dried cakes in nitroglycerin under an air-pump. On exhaustion the air would be removed from the pores of the cakes, and on again admitting the air to the receiver, the nitroglycerin would be forced into and fill up the pores of the clay biscuits. These, after draining, could be rolled up in parchment paper for delivery into commerce. It is thought that in this way the danger of accidental explosions would be materially diminished.

C. H. P.

# PROCEEDINGS

AT THE

# MEETINGS OF THE CHEMICAL SOCIETY,

## SESSION 1875–76.

November 4th, 1875.

Professor Abel, President, in the Chair.

Alfred William Gerrard, Liverpool Road, N.; James B. Guyer, Torquay; Earnest Gee, Southwell, Notts, and A. N. Gow, New Barnet, Herts, were elected Fellows.

The following papers were read:—

"On the Decomposition of Stearic Acid by Distillation under Pressure:" by G. J. Johnston.

"Isomeric Terpenes and their Derivatives." Part V: by C. R. A. Wright and G. H. Beckett.

"On the Alkaloïds contained in the Aconites." Part I: by C. R. A. Wright and G. H. Beckett.

"A Simple Form of Gas Regulator for maintaining a Constant Temperature in Air-baths, Water-baths, Incubators, &c.:" by F. J. M. Page.

"On the Fluorides of Arsenic, Phosphorus, and Iodine:" by R. W. E. McIvor.

"On the Iodides of Antimony:" by R. W. E. McIvor.

"On Tolylphenyl, a New Hydrocarbon:" by T. Carnelley.

November 18th, 1875.

Professor Abel, President, in the Chair.

J. A. P. Price, Wheat Street, Brecon; A. S. McDonald, Merton College, Oxford; A. M. Graham, Plymouth; and W. Davy, Buckhurst Hill, Essex, were elected Fellows.

The following papers were read:—

"On Ethyl-phenyl Acetylene:" by T. M. Morgan.

"Narcotine, Cotarnine, and Hydrocotarnine." Part II: by C. R. A. Wright and G. H. Beckett.

"The Presence of Liquid Carbon Dioxide in Mineral Cavities:" by W. Noel Hartley.

"A Preliminary Notice on the Formation of Coumarin, and of Cinnamic and other similar Acids:" by W. H. Perkin.

December 2nd, 1875.

Professor Abel, President, in the Chair.

W. S. Curptey, Glasgow; J. Kershaw, Southport; G. W. Rawlins, Ramhill, Prescott; A. Boak, Stratford, Essex; R. L. Barnes, Buckhurst Hill; W. E. Hulse, Mincing Lane, E.C.; T. H. Dodd, Royal Arsenal, Woolwich; R. Harvey, Medical College, Madras; J. F. M. H. Stone, St. Peter's College, Cambridge; E. H. Girling, Grenville Street, Brunswick Square; T. McKean, Copland Road, Goran; A. Taylor, South Clerk Street, Edinburgh; T. H. Bland, High Street, Stourbridge; S. Wills, Clifton, Bristol; E. H. Cook, Bristol; J. C. Oman, Agra, India; J. C. Thresh, Eagle Parade, Buxton; A. W. Postans, Baker Street, Portman Square; P. R. Ogle, St. Peter's College, Cambridge; F. C. Desvignes, Hither Green, Lewisham; F. M. Jennings, Cork; and S. A. Prus Syezcpanowski, Anerley, S.E., were elected Fellows.

The following papers were read:—

"On the Decomposition of Alcohol and its Homologues by the Joint Action of Aluminium and its Halogen-compounds:" by J. H. Gladstone and A. Tribe.

"Note on Incense Resin:" by Dr. Stenhouse and C. E. Groves.

"On the occurrence of Native Calcium Chloride at Guy's Cliff, Warwickshire:" by J. Spiller.

"On certain Sources of Error in the ultimate Analysis of Organic Substances containing Nitrogen:" by G. S. Johnson.

"On certain Bismuth Compounds:" by M. M. P. Muir.

"On Bismuthiferous Tesseral Pyrites:" by W. Ramsay.

December 16th, 1875.

Professor Abel, President, in the Chair.

W. Harkness, Somerset House, W.C.; W. A. Stewart, Apothecaries Hall, E.C.; A. Smetham, Stoke Newington, N.; J. D. Mucklow, Sydenham; H. G. Ivery, Melbourne; B. S. Dyer, Burghley

Road, N.W.; A. E. Evans, Kirk Hallam, Derby; G. Cheverton, Tunbridge Wells; and G. H. Bailey, Bowes viâ Darlington, were elected Fellows.

The following papers were read:—

"On Narcotine, Cotarnine, and Hydrocotarnine:" by G. H. Beckett and C. R. A. Wright.

"Action of Potassic Sulphite on the Haloid Derivatives of Phenol:" by H. E. Armstrong and G. Harrow.

"Note on the Action of Nitric Acid on Tribromophenol:" by H. E. Armstrong and G. Harrow.

"On the Sebates of the Alcohol Series:" by E. Neison.

"On some Compounds of Ether with Metallic Chlorides:" by P. P. Bedson.

"Observations on Variations in the Composition of River Waters:" By J. Andrews.

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January 20th, 1876.

Professor Odling, Vice-President, in the Chair.

W. H. Watson, Cumberland; E. H. Gaskell, Highgate, N.; T. Davis, Clapham, S.W.; S. E. Levy, Lancaster Gate, W.; W. Howie, Edinburgh; M. F. Roberts, Hackney, N.E; G. W. Wood, Bow, E.; J. Hargreaves, Warrington; H. W. Hake, Danes Inn, W.C., and H. Glover, Bow, E., were elected Fellows.

The following papers were read:—

"Note on Sebate of Copper:" by E. Neison.

"Narcotine, Cotarnine and Hydrocotarnine. Part IV. On Oxynarcotine—a New Opium Educt and its Relationships to Narcotine and Narceine:" by C. R. A. Wright and G. H. Beckett.

"On a Method of estimating Bismuth volumetrically:" by M. M. P. Muir.

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February 3rd, 1876.

Professor Abel, President, in the Chair.

W. Galbraith, Monmouthshire; D. E. Brown, Newport, Monmouthshire; A. H. Scott White, Nottingham; G. Wilson, Leamington; W. F. Lowe, Hough Green, Chester; S. W. Nockolds, Charing Cross Hospital; G. Haycraft, Faversham; F. J. Lloyd, Barnsbury, N.; H. Allen, Sheffield; F. Isenbart Scard, Blackheath, S.E.; H. B. Dixon, Christ Church, Oxford; and W. A. Smith, Clifton, were elected Fellows.

The following papers were read:—

"On Metachroism, or Colour Change:" by W. Ackroyd.

"On the Formation of Anthrapurpurin:" by W. H. Perkin.

"On Maltose:" by C. O. Sullivan.

"A simple form of Gas Regulator:" by T. Fletcher.

"On high melting points with Special Reference to those of Metallic Salts:" by T. Carnelley.

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February 17th, 1876.

Professor Abel, President, in the Chair.

P. G. Typke, Wimpole Street, Cavendish Square; F. S. Earp, Coventry; H. M. Faber, Oxford; G. Ansdell, Kensington, W.; J. N. Munro, Bristol; N. Bettson Cooke, Irvine, Ayrshire; W. Pearce, Maidenhead, Berks; G. Harrow, Old Bond Street, W.; J. Parry, Ebbw Vale; W. A. Shenstone, Taunton; and C. Williams, Highbury, N., were elected Fellows.

Dr. Frankland delivered a lecture on some points in the Analysis of Potable Waters.

March 2nd, 1876.

Professor Abel, President, in the Chair.

A. B. Prescott, University of Michigan, U.S., and N. Bradley, Manchester, were elected Fellows.

The adjourned discussion on Dr. Frankland's lecture on some points in the Analysis of Potable Waters took place.

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March 16th, 1876.

Professor Abel, President, in the Chair.

J. S. Walton, Bouverie Street, E.C.; J. Head, Yorkshire; J. H. Starling, Erith, Kent; P. J. Winser, Manchester; P. Holland, Lancashire; and A. A. Nesbit, Halstead, Kent, were elected Fellows.

The following papers were read:—

"On Crystallised Glycerin:" by P. van Hamel Roos.

"Notes on the Fatty Acids and on a suggested application of Photography:" by W. H. Hatcher.

"On Stilbene:" by F. Jones.

"On the use of Platinum in the ultimate Analysis of Carbon Compounds:" by F. Kopfer.

"On the action of Organic Acids and their Anhydrides on the Natural Alkaloïds:" Part V.: by G. H. Beckett and C. R. A. Wright.

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March 30th. (Anniversary Meeting).
See vol. i, p. 617.

April 6th, 1876.

Professor Abel, President, in the Chair.

T. B. Udall, Silverdale, Staffordshire, and J. C. Gamble, St. Helen's, Lancashire, were elected Fellows.

The following papers were read:—

"Preliminary Notice on the Action of Sulphuric Acid on Naphthalene:" by Dr. Stenhouse and C. E. Groves.

"On the Action of the Copper-zinc couple on Potassium Chlorate and Perchlorate:" by H. Eccles.

"On Thallium Chlorate:" by J. Muir.

"On Isometric Relations of Thallium:" by T. E. Thorpe.

"On Systematic Nomenclature:" by H. E. Armstrong.

April 20th, 1876.

Dr. Andrews, Vice-President, in the Chair.

Cornelius O'Sullivan, Burton-on-Trent, and Rudolph Messel, Silvertown, Essex, were elected Fellows.

The following paper was read:—

"On the Manufacture of Sulphuric Anhydride:" by Dr. Messel, and Dr. Squire.

The adjourned discussion on Dr. Armstrong's paper on Systematic Nomenclature then took place.

April 28th, 1876. (Special Meeting).

Professor Abel, President, in the Chair.

Dr. Andrews gave a Lecture on Certain Methods of Physico-Chemical Research.

May 4th, 1876.

Dr. Gilbert, Vice-President, in the Chair.

H. C. Jones, Aldersgate Street, E.C.; A. J. Brown, Burton-on-Trent; and Sir David Salomons, Tunbridge Wells, were elected Fellows.

The following papers were read:—

"On Glycero-phosphoric Acid and its Salts as obtained from the Phosphorised Constituents of the Brain:" by Dr. Thudichum and C. T. Kingzett.

"On some Reactions of Biliverdin:" by Dr. Thudichum.

"On the Relation between Chemical Constitution and Colouring Power of Aromatic Substances:" by Otto Witt.

"On Certain Bismuth Compounds." Part II: by M. M. P. Muir.

"A New Method for Preparing the Hydrocarbons Diphenyl and Isodinaphthyl, and on the Action at a High Temperature of Metallic Chlorides on certain Hydrocarbons:" by Watson Smith.

"On the Action of Water and Various Saline Solutions on Copper:" by T. Carnelley.

"Notes on some Experiments made with a view to ascertain the Practical Value of a proposed Method of determining the Mineral Strength of Soils by means of Water Culture:" by G. A. Hight.

May 18th, 1876.

Professor Abel, President, in the Chair.

J. Davidson, Halifax; D. H. Richards, Maesbury, near Oswestry; and W. J. Hanner, Southwold, Suffolk, were elected Fellows of the Society.

Professors Baeyer, Butlerow, Cooke, Friedel, Heintz, and Thomsen were elected Foreign Members of the Society.

The following papers were read:—

"On the Action of Malt Extract on Starch:" by C. O'Sullivan.

"On Metaxenol:" by H. E. Armstrong and Mr. Gaskell.

"On Gases enclosed in Cannel Coal and in Jet:" by J. W. Thomas.

"On Phenomena accompanying the Electrolysis of Water with Oxidisable Electrodes:" by J. H. Gladstone and A. Tribe.

"On the Estimation of Hydrogen Occluded by Copper, with Special Reference to Organic Analysis:" by Dr. Thudichum and H. W. Hake.

June 1st, 1876.

Professor Abel, President, in the Chair.

R. H. Harland, Bow, E.; J. Edmands, Savile Row, W.; H. Holcroft, Wolverhampton; C. A. Buckmaster, Wandsworth, S.W.; S. Hall, Bow, E.; P. C. Gilchrist, Blaenavon, Monmouthshire; and W. Hibbert, Royal Institution, W., were elected Fellows.

The following papers were read:—

"On Hemine, Hematine, and a Phosphorised Substance contained in Blood Corpuscles:" by Dr. Thudichum and C. T. Kingzett.

"On Variations in the Critical Point of Carbon Dioxide in Minerals, and Deductions from these and other Facts:" by W. N. Hartley.

"On some Trials of Frankland and Armstrong's Combustion Process in Vacuo:" by Dr. Thudichum and C. T. Kingzett.

"On Peroxides, on Chromic and Perchromic Acids, and on the Estimation of Nitrogen:" by T. Fairley.

"On Aluminium Nitride, and the Action of Aluminium on Sodium Carbonate at High Temperatures:" by J. W. Mallet.

"On the Volumetric Estimation of Mercury:" by R. V. Tuson and E. Neison.

June 15th, 1876.

Dr. Gladstone, Vice-President, in the Chair.

A. B. Cortis, Worthing, Sussex; G. F. Thomson, Middlesbrough; J. Heron, Shepherd's Bush, W.; C. G. Matthews, Beckenham; G. Evans, Llanelly, South Wales; and Otto N. Witt, Brentford, were elected Fellows.

The following papers were read:—

"Chemical Studies:" by J. Dewar.

"Researches on the Reduction of Nitric Acid and on the Oxides of Nitrogen. Part. I. On the Gases evolved by the Action of Metals on Nitric Acid:" by J. Ackworth and H. E. Armstrong.

"On an Alkaloïd obtained from Jaborandi, its Platinic Compound, and their Formulæ:" by C. T. Kingzett.

"The Simultaneous Action of Iodine and Aluminium on Ether and Compound Ethers:" by J. H. Gladstone and A. Tribe.

"On some Compounds of Antimony Pentachloride with Alcohols and with Ether:" by W. C. Williams.

"On the Volatility of Barium, Strontium, and Calcium:" by J. W. Mallet.

"On the Action of Chlorine on Acetamide:" by E. W. Prévost.

"Note on the Perbromates:" by M. M. P. Muir.

"On a New and Convenient Form of Ureometer:" by J. G. Blackley.

Donations to the Library, Session 1875–76:—

"The Complete Works of Count Rumford; published by the American Academy of Arts and Sciences:" from the Academy.

"Air, and its relation to Life:" by W. N. Hartley: from the Author.

"Attfield's Chemistry," 6th Edition: from the Author.

"Lecture Notes for Chemical Students, Vol. I. Inorganic Chemistry:" by E. Frankland: from the Author.

"The Elements of Chemical Analysis. Inorganic and Organic:" by E. A. Parnell. 1st Edition: from Trenham Reeks, Esq.

"Quantitative Chemical Analysis:" by R. Fresenius. 7th Edition: edited by Arthur Vacher: from the Editor.

"Adulterations of Food, with short processes for their Detection:" by Rowland J. Atcherley, Ph.D.: from the Author.

"Revelations of the Spectrum:" by E. Vogel: from the Author.

"Illustrations of the Centimeter-Gram-Second System of Units:" by Prof. Everett: from the Author.

"The Faraday Lecture, 1875:—The Lifework of Liebig in Experimental and Philosophic Chemistry:" by Dr. A. W. Hofmann: from the Author.

"On Milk in Health and Disease:" by A. H. Smee: from the Author.

"Dyeing and Calico-printing:" by the late Dr. F. Crace-Calvert: edited by Dr. Stenhouse and C. E. Groves, Esq.: from the Publishers.

"Digest of Reported Cases relating to the Law and Practice of Letters Patent for Inventions:" by Clement Higgins: from the Author.

"Report on the Explosion of Gunpowder in the Regent's Park on the 2nd of October, 1874:" by Major Majendie, R.A.: from F. A. Abel, Esq.

"Sixth Report of the Rivers' Commission (1868). Domestic Water Supply of Great Britain: from Dr. Frankland.

"Angola and the River Congo." 2 Vols. 8vo.: by J. J. Monteiro: from the Author.

"Lehrbuch der Chemie: von J. J. Berzelius; aus dem Schwedischen übersetzt: von F. Wöhler, 7 Bände: from G. H. Wollaston, Esq.

"Handbuch der Mineralchemie:" von C. F. Rammelsberg. 2te. Auflage, 1870: from the Author.

"Die Pflanzenfaser und ihre Aufbereitung für die Technik:" von Dr. Hugo Müller: from the Author.

Pamphlets:—

"The Repulsion of Solid Bodies referable to Radiation:" by the Rev. J. A. Stevens: from the Author.

"Experiments with the alleged New Force:" by G. M. Beard, M.D.: from the Author.

"Optical Notices:" by Wolcott Gibbs: from the Author.

"On the effects of Heat on Iodide of Silver:" by G. F. Rodwell: from the Author.

"On the Coefficient of Expansion of Paraffin of a High Boiling Point:" by G. F. Rodwell: from the Author.

"Liquid Carbonic Acid, its Preparation, and the Construction of Vessels to contain it:" by Walter N. Hill: from the Author.

"The Composition of the Ammonium Amalgam:" by R. Routledge: from the Author.

"On the Hexatomic Compounds of Cobalt:" by Wolcott Gibbs: from the Author.

"Melanosiderite, a new Mineral Species, from Mineral Hill, Delaware, Co. Pennsylvania:" by J. P. Cooke, jun.: from the Author.

"On the varieties of Vermiculite:" by J. P. Cooke, jun. from the Author.

"The Rocks of the Mining Districts of Cornwall and their relation to Metalliferous Deposits:" by J. Arthur Phillips: from the Author.

"The Physical Features of the Valley of the Minnesota River, and their Signification:" by E. K. Warren: from the Author.

"On the Geological Conditions affecting the Water-supply to Houses and Towns, with special reference to the mode of supplying Oxford:" by Joseph Prestwich, M.A.: from the Author.

"Note on the Occurrence of 'Fairy-rings:'" by Dr. J. H. Gilbert: from the Author.

"On the Chemical Composition of Phosphatic Minerals used for Agricultural Purposes:" by Dr. Voelcker: from the Author.

"On the Manufacture of White Caustic Soda:" by G. E. Davis: from the Author.

"Hargreaves and Robinson's Process for the Manufacture of Sulphates:" by James Hargreaves: from the Tyne Chemical Society.

"On the Immediate Results of the Operation of the 'Glasgow Improvement Trust,' as regards the Inhabitants displaced, with

remarks on the Question of Preventing the Evils which the Trust seeks to remedy:" by Dr. J. B. Russell:

from the Philosophical Society of Glasgow.

"Ueber den Einfluss des Freiherrn Justus von Liebig auf die Entwickelung der reinen Chemie:" von E. Erlenmeyer:

from the Royal Bavarian Academy of Sciences.

"Ueber die Beziehungen der Chemie zur Rechtspflege:" von L. A. Buchner: from the Royal Bavarian Academy of Sciences.

"Untersuchungen über Unterchlorsäure und Euchlorin:" von F. Pebal: from the Author.

"Sur une Combinaison de l'Acide Picrique avec l'Anhydride Acetique:" par D. Tommasi and H. David.

"Etude Chimique sur la Source Sulfurée Sodique forte et iodobromurée de Challis (Savoie): par le Docteur F. de Garrigou:

from the Author.

"Discorso di Apertura della Classe III, del 1° Congresso della Sociétá italiana per il progresso delle Scienze:" de Prof. Cannizaro.

"La Chimica al xii Congresso degli Scienziati italiani riunitasi a Palermo:" from Professor Paternò.

Periodicals:—

"Philosophical Transactions for 1875:" from the Royal Society.

"List of Officers and Fellows of the Royal Society for 1875:"

from the Royal Society.

"Memoirs of the Royal Astronomical Society," Vol. xl:

from the Society.

"Monthly Notices of the Royal Astronomical Society, 1875-76:"

from the Society.

"Proceedings of the Royal Institution of Great Britain," Vol. ix: from the Institution.

"Reports of Friday Evening Lectures at the Royal Institution, 1876:" from the Institution.

"Quarterly Journal of Science," Vol vii: from the Editor.

"Quarterly Journal of the Geological Society, 1875—76:"

from the Society.

"Journal of the Iron and Steel Institute, 1876:"

from the Institute.

"Year-book of Pharmacy, 1875:" from Professor Attfield.

"Pharmaceutical Journal and Transactions." Third series, Vol vi:

from the Pharmaceutical Society.

"The Photographic Journal, 1875-76:"

from the Photographic Society.

"Journal of the Society of Arts, 1875-76:" from the Society.

"The Textile Colourist." Edited by Charles O'Neile, F.C.S., Vol. i, 1876: from the Editor.

"Nature, 1875–76:" from the Editor.

"The Chemical News, 1875–76;" from the Editor.

"The Telegraphic Journal, 1875–76:" from the Editor.

"Engineering, 1875–76:" from the Editor.

"Electrical News, 1876:" from the Editor.

"The Druggist:" from the Editor.

"The Chemist and Druggist:" from the Editor.

"The Chemist and Druggist's Advocate, 1875–76:" from the Editor.

"The Western:" new series, 1876: from the Editor.

"Practical Magazine, 1875–76:" from the Editor.

"Journal of the Liverpool Polytechnic Society, Dec. 18, 1875:" from the Society.

"Proceedings of the Philosophical Society of Glasgow, 1874–75:" from the Society.

"Glasgow University Calendar, 1875–76:" from the University.

"Transactions of the Royal Irish Academy." Vol. xxv. Parts V to XIX: from the Academy.

"Proceedings of the same." Vol. i; No. IX. Vol. ii; Nos. I—III: from the Academy.

"American Journal of Science and Arts." Vols. x, xi: from the Editors.

"Journal of the Franklin Institute." Third Series. Vols. lxxi, lxxii: from the Institute.

"Transactions of the American Philosophical Society." Vol. xv. Part II. (1875): from the Society.

"Proceedings of the American Philosophical Society, January to June, 1875:" from the Society.

"Smithsonian Report for 1875:" from the Smithsonian Institution.

"Monthly Reports of the Department of Agriculture (U.S.) for 1874 and 1875:" from the Department.

"Transactions of the Wisconsin Academy of Sciences, Arts, and Letters." Vol. ii; 1873–74: from Alfred Sener, Esq.

"Archives of Science." Vol. i No. VI: from the Orleans County Society of Natural Sciences, Vermont (U.S.).

"Bulletin of the Bussy Institution, Boston:" from the Institution.

"Moniteur Scientifique, 1875–76:" from the Editor.

"Revue Scientifique:" from the Editor.

"Les Mondes, 1875–76:" from the Editor.

"Mémoires de l'Académie des Sciences et Lettres de Montpellier." Section des Sciences. Tomes vii, viii: from the Academy.

"Bulletin de l'Académie Royale des Sciences de Belgique, 1874–1875–1876:" from the Academy.

"Annuaire de l'Académie Royale des Sciences de Belgique, 1875–1876:" from the Academy.

"Bulletin de la Société Industrielle et Agricole d'Angers et du Département de Maine et Loire, 1875." 1er Trimestre:
from the Society.

"Memorie dell Accademia delle Scienze dell' Instituto di Bologna." Serie 3. Tomi iii, iv: from the Academy.

"Rendiconti delle Sessioni della stessa Accademia, 1873-74:"
from the Academy.

"Denkschriften der Kaiserlichen Akademie der Wissenschaften." 34-ter Band: from the Academy.

"Sitzungsberichte derselben," 1874. Zweite Abtheilung, Nos. 8—10. 1875; Zweite Abtheilung, Nos. 1—5.

"Abhandlungen der Königlich-Bayerischen Akademie der Wissenschaften. 12-ter Band. Erste Abtheilung. 1875:
from the Academy.

"Jenaische Zeitschrift fürNaturwissenschaft." 12-ter Band. Supplement: from the Editor.

"Muster-Zeitung, Zeitschrift für Färberei, Druckerei, Bleicherei, u. s. w. No. 39 (1875): from the Editor.

"Verhandlungen der Naturforschenden Gesellschaft in Basel." 6-ter Theil. 2-ter Heft (1875): from the Society.

"Verhandlungen der Physikal-Medicinischen Gesellschaft zu Würzburg." 9-ter Band. 1 und 2 Heft: from the Society.

"Mandblaad voer Naturwetenschappen, 1875-76:"
from the Philosophical Society of Amsterdam.

"Oversigt over det Kongelige Danske Viderskabernes Selskabs." Forhandlinger, og des Medlemmers Arbeeten:
from the Royal Danish Academy of Sciences.

The following books have been presented by Arthur Vacher, Esq.:—

"The Chemical Catechism:" by Samuel Parkes. 12th edition.

"A System of Theoretical and Practical Chemistry:" by F. Accum.

"The First Principles of Chemical Philosophy:" by J. P. Cooke, Jun.

"Practical Pharmacy:" by F. Mohr and Th. Redwood.

"Muspratt's Chemistry."

"The Natural Laws of Husbandry:" by Justus von Liebig.

"Jacquemin's Chemistry:" translated from the German.

"A Manual of Chemical Physiology:" by J. L. W. Thudichum.

"The Pathology of the Urine:" by J. L. W. Thudichum.

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